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Carbonatite diversity in the Central Andes: the Ayopaya alkaline province, Bolivia

Abstract The Ayopaya province in the eastern Andes of Bolivia, 100 km NW of Cochabamba, hosts a Cretaceous alkaline rock series within a Palaeozoic sedimentary sequence. The alkaline rock association comprises nepheline-syenitic/foyaitic to ijolitic intrusions, carbonatite, kimberlite, melilititic, nephelinitic to basanitic dykes and diatremes, and a variety of alkaline dykes. The carbonatites display a wide petrographic and geochemical spectrum. The *Cerro Sapo* area hosts a small calciocarbonatite intrusion and a multitude of ferrocarbonatitic dykes and lenses in association with a nepheline-syenitic stock. The stock is crosscut by a spectacular REE-Sr-Th-rich sodalite-ankerite-baryte dyke system. The nearby *Chiaracke* complex represents a magnesiocarbonatite intrusion with no evidence for a relationship to igneous silicate rocks. The magnesiocarbonatite (Σ REE up to 1.3 wt%) shows strong HREE depletion, i.e. unusually high La/Yb ratios (520–1,500). Calciocarbonatites (Σ REE up to 0.5 wt%) have a flatter REE distribution pattern (La/Yb 95–160) and higher Nb and Zr contents. The sodalite-ankerite-baryte dyke system shows geochemical enrichment features, particularly in Na, Ba, Cl, Sr, REE, which are similar to the unusual natrocarbonatitic lavas of the recent volcano of Oldoinyo Lengai, Tanzania. The Cerro Sapo complex may be regarded as an intrusive equivalent of natrocarbonatitic volcanism, and provides an example for carbonatite genesis by late-stage crystal fractionation and liquid immiscibility. The magnesiocarbonatite intrusion of Chiaracke, on the other hand, appears to result from a primary carbonatitic mantle melt. Deep seated mantle magmatism/metasomatism is also expressed by the occurrence of a kimberlite dyke. Neodymium and strontium isotope data (ε_{Nd} 1.4–5.4, $^{87}Sr/^{86}Sr$ < Bulk Earth) indicate a depleted mantle source for the alkaline magmatism. The magmatism of the Ayopaya region is attributed to failed rifting of western South America during the Mesozoic and represents the only occurrence of carbonatite and kimberlite rocks in the Andes.

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Introduction

The formation of carbonatite melts is much debated. There is experimental evidence for (1) direct generation of carbonatitic melts by very low degree of partial melting in the mantle, as well as for low-pressure magmatic differentiation of carbonated silicate melts, i.e. (2) liquid immiscibilty and (3) crystal fractionation (see, among many others, discussion in Harmer and Gittins 1997; Bell et al. 1998; Bell and Tilton 2001). All three petrogenetic processes are supported by petrological field studies on different carbonatite occurrences (e.g. Bailey 1993; Bell and Keller 1995; Cooper and Reid 1998; Harmer and Gittins 1998; Veksler et al. 1998a). The recent discovery of magnesio- and calciocarbonatites within a few kilometer distance in the Bolivian Andes, together with a wide alkaline rock spectrum, underlines the diversity of the carbonatite family and the coexistence of primary magnesiocarbonatite mantle melts, and of calciocarbonatite exsolved from carbonated nepheline-syenitic melts. Extreme crystal fractionation is documented by
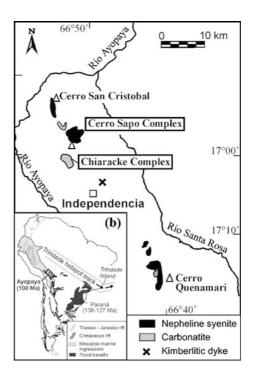
a late sodalite-ankerite-baryte dyke system, which has no known equivalent elsewhere, but shares some petrochemical features of the unique Oldoinyo Lengai natrocarbonatite.

The present study was initiated by the discovery of alluvial diamonds in the Ayopaya region (Lehmann and Schultz 1999). Field work during the last years identified a carbonated kimberlite dyke (see below), but microdiamond testing of a 30-kg-bulk sample of the dyke proved negative and a direct link to diamonds could not be proven so far. In the following sections we will give an overview of the petrology and the geochemistry of the most important magmatic rock types of the Ayopaya alkaline province, with focus on potential diamond-bearing rocks and carbonatite petrogenesis, especially on the Chiaracke carbonatite intrusion and the multiple Cerro Sapo alkaline complex. We will place the Ayopaya alkaline province in a regional tectonic context and will discuss a petrogenetic model for the rock spectrum studied.

Geological setting

The Ayopaya alkaline province is situated in the eastern Andes of Bolivia, near Independencia, about 150 km SE of La Paz and 100 km NW of Cochabamba. It forms a 50×15 km, NW–SE trending belt between the Santa Rosa and Ayopaya rivers (Fig. 1). The steep landscape is characterised by altitudes from 1,500 to 4,400 m a.s.l. and dense subtropical vegetation reaching up to 3,500 m. Alkaline rocks in the Ayopaya region were first reported by Ahlfeld and Wegener (1931) and Ahlfeld and Mosebach (1935). Ahlfeld rediscovered the spectacular sodalite occurrence of the Cerro Sapo, which had been mined from pre-Incaic to Incaic times. Sodalite gemstones from the Ayopaya region have been found at Tiahuanaco and other historical sites in South America (Ahlfeld and Wegener 1931; Brendler 1932).

The Ayopaya alkaline province is part of a Mesozoic intracontinental rift zone (Fig. 1) stretching from Peru to SE Argentina. Rifting started in Peru in the late Permian to early Jurassic (Ramos and Aleman 2000; Sempere et al. 2002), and reached Argentina in the Cretaceous (Viramonte et al. 1999). The main phase of rifting in Bolivia coincides with a decrease in the magmatic activity in the arc in between 120 and 80 Ma (Hammerschmidt et al. 1992). This period was characterised by a reorganisation of the oceanic plates in the eastern Pacific Ocean, and the subduction direction of

Fig. 1 Location of major alkaline intrusive units of the Ayopaya alkaline province. Inset with sketch map of large-scale rifting of South America during the Cretaceous (compiled from Ramos and Aleman 2000; Avila Salinas 1989; Jaillard et al. 2000; Tompkins and Gonzaga 1989; Sempere et al. 1998). The intracontinental Cretaceous evolution of South America represents failed rifts on a convergent margin. During the Andean orogeny parts of the rift system, such as in Ayopaya, were inverted and eroded. The Cretaceous kimberlites and alkaline complexes of central Brazil (e.g. Alto Paranaiba, Juína) are related to mantle plume activity which presently is situated under Trindade Island (Gibson et al. 1995)

the Pacific lithosphere changed fundamentally from SE to NE (e.g. Scheuber et al. 2000).

Potassium–Argon isotope data on phlogopite megacrysts from ultramafic breccia (100.7 ± 1.2 Ma) and lamprophyre (99.0 ± 1.1 Ma) define a Cretaceous age for the magmatic rock sequence (Table 1). This is in agreement with earlier results by Kennan et al. (1995) who dated a phlogopite megacryst from the Laguna Khoallaqui, 6 km NW of Independencia (Fig. 1) at 98 ± 3 Ma.

The igneous rock suite of the Ayopaya province comprises a great variety of alkaline, predominantly sodic, rocks consisting of nepheline syenite to foyaite stocks, carbonatite intrusions and dykes, ultramafic breccias and dykes of melilititic–nephelinitic composi-

Table 1 K–Ar age data for dark mica from ultramafic breccia (I6a and AR-1) and a lamprophyre sample (I15)

Sample	Location	Sample material	K (wt %)	rad. Ar. (nl/g)	rad. Ar (%)	Age (Ma)
I 6a	Laguna Khoallaqui	Phlogopite megacryst	7.84	31.8	91.0	100.7 ± 1.2
I 15	Khori-Mayu	Biotite megacryst	7.62	30.2	92.4	99.0 ± 1.1
AR-1	Laguna Khoallaqui	Phlogopite megacryst	7.87	30.7	–	97.7 ± 2.8

Data on AR-1 from Kennan et al. (1995: 169). Decay constants are from Steiger and Jäger (1977)

tion and a kimberlitic dyke near the village of Independencia (Figs. 1 and 2). Small dykes and sills of basanite, tephrite, phonolite and lamprophyre are widespread in the entire Ayopaya region. The nepheline syenitic stocks of the Cerro Sapo and the Cerro San Cristobal are intimately associated with small carbonatitic intrusive bodies and dykes (Fig. 1). Additionally, the Cerro Sapo complex hosts a spectacular sodalite-ankerite-baryte dyke system (Figs. 2 and 3). In contrast to the Cerro Sapo complex the Chiaracke carbonatite intrusion shows no relation to magmatic silicate rocks.

The country rocks of the alkaline intrusions consist of very-low-grade metamorphic Ordovician to Devonian shales and sandstones (Kley et al. 1997). This more than 10-km-thick clastic sequence forms the backbone of the Eastern Andes of Bolivia.

Analytical methods

Major and most trace elements were measured by X-ray fluorescence spectrometry on lithium metaborate fused disks at Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover (Tables 2, 3 and 4). Rare-earth elements were measured by inductively-coupled plasma mass spectrometry (ICP-MS) at Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, and at GeoForschungsZentrum Potsdam. Some samples were also analysed by ICP-MS for Sc, Cs, Pb, Th and U.
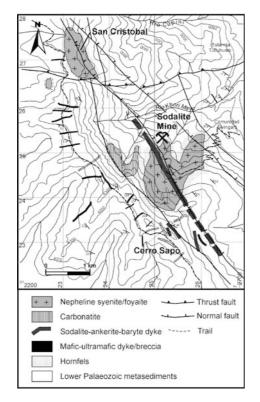
These data are given in three-digit numbers. The digestion of samples for ICP-MS was by $HF/HClO_4$ in Teflon beakers at 200°C and followed standard procedures. F
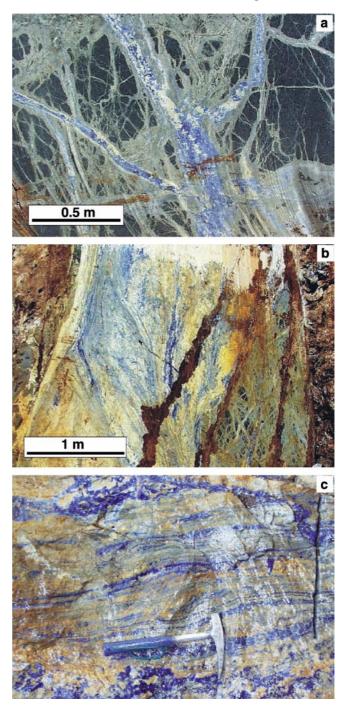

Fig. 3 Rock textures in the sodalite–ankerite–baryte dyke. **a** Sodalite–ankerite stockwork in syenitic host rock. Veinlets of sodalite (*blue*) and ankerite (*yellow*) surrounded by narrow zones of fenitisation (*greenish-grey* bleached). Outcrop at the mining face of the sodalite mine in the immediate hanging wall of the sodalite–ankerite dyke. **b** Fluidal texture consisting of narrow sodalite-ankerite flow-banding in the sodalite-ankerite dyke system. Picture taken from the stope of the Cerro Sapo sodalite mine. **c** Narrow layering of sodalite (*dark blue*) and ankerite (*yellow*) indicating rhythmic crystallisation from a highly fractionated carbonated silicate system

Fig. 2 Geological map of the Cerro Sapo alkaline complex (modified after Balderrama Zárate 2003)

Table 2 Major and trace element composition of the major alkaline silicate rocks of Ayopaya

	Cerro Sapo				Cerro San Cristobal		Quenamari
	Ijolite I39	Foyaite I30	Ne syenite I44	Sodalite AY25	Hbl syenite I34	Foyaite I126	Ne syenite I46
SiO_2 (wt %)	44.1	53.2	52.9	37.0	55.6	56.15	44.4
TiO_2	2.10	0.75	0.42	0.07	0.85	0.18	2.56
Al_2O_3	14.6	21.2	20.7	31.6	18.8	21.34	16.4
ΣFe_2O_3	11.2	4.23	3.86	0.28	6.37	2.45	10.3
MnO	0.188	0.138	0.199	0.021	0.172	0.111	0.174
MgO	8.24	0.54	0.22	0.07	2.03	0.14	4.11
CaO	10.1	2.64	1.80	0.33	3.70	0.97	7.81
Na_2O	4.86	9.17	9.0	24.4	6.22	8.96	4.69
K_2O	2.45	5.70	5.56	0.44	4.25	6.24	3.14
P_2O_5	0.46	0.12	0.06	0.04	0.27	0.06	0.92
Cl	0.100	0.342	0.956	4.55	0.104	NA	0.016
F	0.125	0.035	0.056	< 0.05	0.088	NA	0.104
LOI	0.86	1.29	2.29	1.02	1.21	1.84	4.77
Total	99.4	99.3	98.0	99.7	99.6	98.4	99.4
Sc (ppm)	19	4	< 2	< 2	6	0.3	10
V	223	38	19	10	57	14	193
Cr	328	< 3	7	7	63	6	30
Co	51	4	10	< 3	18	1	44
Ni	158	< 3	< 3	< 3	29	2	22
Cu	52	14	15	35	22	2	22
Zn	115	76	106	287	130	206	106
Ga	22	25	34	50	25	32	19
As	5	3	18	11	8	18	4
Br	NA	NA	NA	300	NA	27	NA
Rb	97	203	200	6	200	301	113
Sr	833	1,519	874	812	582	613	866
Y	24	19	47	19	27	12	26
Zr	271	304	457	< 3	514	297	249
Nb	124	183	218	30	139	55	121
Mo	12	2	81	5	5	< 5	14
Sn	< 2	5	< 2	< 2	5	< 2	< 2
Cs	< 5	< 5	< 5	< 5	10	12.9	< 5
Ba	920	1,486	610	4,426	732	849	1,115
La	67.3	27.8	199	68.0	61.8	25.7	62.4
Ce	123	59.3	255	140	124	35.8	118
Pr	13.3	6.7	NA	NA	10.5	3.0	13.1
Nd	48.3	24.5	NA	NA	33.3	8.0	49.7
Sm	8.6	4.3	NA	NA	5.4	1.1	8.91
Eu	2.5	1.3	NA	NA	1.2	0.3	2.62
Gd	7.5	3.7	NA	NA	4.7	0.87	7.88
Tb	1	0.56	NA	NA	0.73	0.14	1.05
Dy	5.5	3.1	NA	NA	4.3	0.86	5.59
Ho	0.97	0.57	NA	NA	0.83	0.17	1.00
Er	2.6	1.7	NA	NA	2.6	0.52	2.77
Tm	0.34	0.25	NA	NA	0.40	0.08	0.38
Yb	2.2	1.8	NA	NA	2.7	0.61	2.25
Lu	0.31	0.30	NA	NA	0.43	0.10	0.35
Ta	9	5	14	< 5	9	4	9
W	14	< 5	15	< 5	8	8	9
Pb	< 4	25	39	58	15	101	< 4
Th	11	5	48	96	27	21	5
U	8	6	23	< 3	9	7	7
(Na + K)/Al	0.73	1.03	1.03	1.10	0.82	1.05	0.70
Mg#	0.57	0.19	0.09	0.31	0.36	0.09	0.42

NA not analysed

was determined by H_3PO_4 distillation and ion-selective electrode; CO_2 by colorimetric titration.

Most of the Sr and Nd isotope analyses were done at the Laboratory of Isotopic Geochronology and Geochemistry of the Institute of Precambrian Geology and Geochronology, St Petersburg, Russia (Table 5). The measurements were performed on a Finnigan MAT-261 mass spectrometer equipped with eight collectors under static mode. The $^{143}Nd/^{144}Nd$ ratio was normalised within-run to $^{148}Nd/^{144}Nd = 0.241570$ and adjusted to a $^{143}Nd/^{144}Nd$ value of 0.511860 for La Jolla. Repeat measurements of $^{143}Nd/^{144}Nd$ ratio of the La Jolla standard varied from 0.511875 to 0.511912 with a mean value of 0.511894 ± 10 ($n = 57$). Sr isotope composition

Table 3 Major and trace element composition of the carbonatite rock suite of Ayopaya

	Chiaracke (Magnesiocarbonatite)							Dykes and lenses			Cerro Sapo Calciocarbonatite			Sodalite-ankerite-baryte dyke			Cristobal [Calciocarbonatite]	Diatreme
	I74	I78	I79	I80	I81	I82	I83	I22	I23	I123	140	I53a	I62	AY24	AY11	AY12	I127b	I70a
SiO_2 (wt %)	2.27	0.14	0.70	0.71	<0.1	<0.1	0.54	8.75	13.7	6.44	0.30	2.16	1.25	15.8	23.2	12.9	1.36	4.98
TiO_2	0.006	0.004	0.007	0.007	0.017	0.003	0.035	0.168	0.199	0.663	0.042	0.143	0.016	0.002	<0.001	0.010	0.015	1.38
Al_2O_3	0.14	<0.05	<0.05	0.47	0.06	<0.05	<0.05	2.63	4.04	1.84	0.10	0.13	<0.05	10.9	10.4	11.5	0.33	1.37
ΣFe_2O_3	9.9	8.8	24.1	12.4	6.04	9.3	42.8	15.0	13.7	14.6	3.41	4.22	3.52	14.0	11.7	12.7	3.75	19.3
MnO	2.20	1.60	2.94	1.61	1.05	2.17	4.52	3.02	2.53	2.02	0.915	0.812	0.231	1.12	0.919	0.997	0.772	0.991
MgO	23.6	17.0	20.6	16.6	17.3	14.8	5.87	6.71	7.49	6.18	0.71	1.13	0.25	4.00	3.43	4.07	0.48	7.25
CaO	17.1	27.3	4.96	19.1	28.7	28.8	10.9	24.8	21.3	23.2	48.3	47.1	51.1	16.5	12.9	15.9	49.1	25.0
Na_2O	0.06	0.03	0.08	0.1	<0.01	0.03	0.16	0.08	0.51	0.14	0.11	0.65	0.20	4.35	6.24	8.34	0.07	0.15
K_2O	0.16	0.03	0.03	0.08	0.01	0.01	0.04	1.93	2.41	1.39	0.03	0.06	0.08	0.18	0.07	0.17	0.19	0.89
P_2O_5	0.431	0.012	1.03	2.81	0.757	0.079	0.904	0.478	0.107	0.073	1.30	0.329	3.22	0.180	0.030	0.290	0.099	0.068
CO_2	40.9	44.1	37.8	36.8	44.7	43.5	19.2	32.5	32.8	32.9	41.0	40.7	38.3	27.1	23.4	27.5	41.1	35.7
F	1.33	0.113	0.267	0.721	0.189	0.505	0.259	0.085	0.055	0.269	0.133	0.140	0.317	0.155	n.a.	n.a.	0.083	0.118
SO_3	0.47	0.05	2.52	2.95	0.07	0.51	2.67	2.38	0.85	2.26	0.28	1.86	2.68	1.18	0.46	0.56	0.86	0.64
Total	98.5	99.1	95.0	94.4	98.9	99.7	87.9	98.5	99.7	91.9	96.6	99.4	101.1	95.5	92.7	94.9	98.2	97.9
Sc (ppm)	33.9	30.8	7.1	31.5	14	9.6	22.6	48	36	9	4.7	4.6	1.7	58	23.6	24.6	8.0	40.4
V	195	84	38	96	104	21	33	242	170	144	32	183	217	117	61	68	18	420
Cr	4	13	5	43	<2	<2	14	218	211	148	<3	18	13	133	85	111	10	197
Co	5	3	3	6	2	2	15	9	14	25	7	8	12	9	15	12	7	41
Ni	2	4	8	21	4	2	2	42	36	82	<3	4	2	35	31	26	4	103
Cu	3	2	2	2	2	2	2	19	27	147	<10	2	11	688	156	94	2	2
Zn	1,311	161	365	99	94	289	2,620	959	3,860	18,300	27	262	43	6,670	2,707	882	154	544
Ga	<2	<2	<2	<2	<2	<2	<2	<3	6	5	<2	9	<2	15	10	19	<2	<2
As	5	6	24	<2	<2	<2	<2	46	11	33	11	17	<2	25	<2	<2	<2	15
Rb	55	2	5	7	9	4	4	50	76	51	<2	12	16	<2	<20	<20	17	8
Sr	6,300	824	1,770	1,940	665	965	11,690	4,870	5,230	31,810	14,500	19,750	16,640	18,710	14,430	12,220	14,660	1,560
Y	92	87	79	257	109	117	94	131	90	632	201	171	36	315	176	204	69	188
Zr	56	27	52	63	26	27	240	267	186	1,050	439	489	367	462	1.4	1.1	317	48
Nb	144	8	14	168	40	86	596	52	43	298	2,025	1,743	37	4	10	14	777	1,552
Mo	5	<5	46	14	14	<5	49	59	10	<2	<5	<5	<5	<2	<5	<5	7	<5
Sn	<5	<5	11	7	9	<5	22	12	2	6	<5	<5	<5	<5	<5	17	<5	18
Cs	0.49	0.07	0.05	0.09	0.09	0.03	0.09	9	6	21	10	16	0.06	41	26	<0.5	0.04	0.08
Ba	2,560	156	50,950	65,260	616	10,210	104,100	11,390	3,430	14,870	8,750	5,410	1,100	3,890	19,450	10,720	1,620	14,910
La	1,727	1,451	1,138	2,119	3,790	30.0	646	585	509	1,871	1,350	1,220	224	711	519	487	819	621
Ce	3,516	2,581	2,673	3,469	6,560	116	2,064	1,649	1,398	3,426	2,310	1,847	331	1,530	1,150	1,050	1,554	1,181
Pr	397	257	327	352	695	17.4	338	186	165	414	218	187	32.4	196	153	142	163	138
Nd	1,371	852	1,075	1,190	2,140	66.8	1,084	715	652	2,134	741	640	93.6	719	638	603	539	570
Sm	182	102	129	176	252	15.5	105	178	195	2,184	114	88.8	11.7	191	167	170	65.6	585
Eu	44.6	24.0	32.1	49.7	52.8	3.69	27.6	52.2	60.3	712	33.4	26.7	3.20	67.9	55.2	59.8	15.9	241
Gd	95.1	53.1	68.2	114	162	15.8	54.0	139	148	1,574	93.1	62.8	8.30	206	166	177	31.3	571
Tb	8.68	4.98	6.81	11.70	10.1	2.82	5.70	13.4	12.1	97.0	11.3	7.06	0.94	27.2	20.0	22.2	2.77	32.4
Dy	28.3	18.0	23.0	47.0	37.7	16.9	19.9	45.7	37.0	219	49.1	33.0	4.43	119	83.3	101	11.5	64.9
Ho	3.25	2.23	2.68	5.90	4.10	3.18	2.31	5.15	3.57	16.4	7.70	5.09	0.82	14.4	9.40	11.2	1.90	4.86
Er	5.10	3.54	3.96	8.82	7.7	8.22	3.69	9.72	4.79	14.5	19.6	12.2	2.19	21.6	12.3	14.8	5.17	2.95
Tm	0.48	0.31	0.38	0.74	0.70	1.05	–	0.86	0.38	1.00	2.35	1.38	0.32	1.80	0.70	0.90	0.78	0.59

Table 3 (Contd.)

	Chiaracke (Magnesiocarbonatite)							Dykes and lenses			Cerro Sapo Calciocarbonatite			Sodalite–ankerite–baryte dyke			Cristobal [Calciocarbonatite]	Diatreme
	I74	I78	I79	I80	I81	I82	I83	I22	I23	I123	140	153a	I62	AY24	AY11	AY12	I127b	I70a
Yb	2.61	1.80	1.95	4.10	2.5	5.61	2.35	5.01	1.89	3.5	14.2	7.65	1.91	9.30	2.10	2.40	5.38	2.72
Lu	0.55	0.38	0.69	–	0.40	0.69	–	0.71	0.38	–	1.99	1.02	0.30	1.20	0.20	0.30	0.81	b.d.
Ta	<1	<1	<1	<1	<1	<1	<1	8	<5	<1	<5	<1	8	<1	<1	<1	<1	6
Pb	18	18	10	7	34	7	111	560	300	1,620	11	35	14	2,645	19	56	48	69
Th	240	277	405	817	600	30	323	405	433	6,040	<5	34.4	1.5	2,033	1,440	1,380	26.4	1,612
U	3.52	0.04	0.12	0.41	0.55	0.16	0.01	3	<3	<3	5.00	1.31	1.44	0.6	0.8	0.9	6.33	1.55
Ca#	0.46	0.66	0.22	0.58	0.66	0.70	0.69	0.81	0.77	0.82	0.99	0.98	1.00	0.83	0.82	0.82	0.99	0.80
Mg#	0.81	0.78	0.60	0.70	0.84	0.74	0.20	0.44	0.49	0.43	0.27	0.32	0.11	0.34	0.34	0.36	0.19	0.40

Low totals in the sodalite–ankerite dyke are due to high chlorine content (not analysed) and high trace element contents (e.g. Sr, Ba).
NA not analysed

was normalised within-run to $^{88}Sr/^{86}Sr = 8.37521$. The value of Sr isotope standard SRM-987 during this work was $^{87}Sr/^{86}Sr = 0.710248 \pm 15$ (2σ, 16 runs). Assigned errors (2σ) for $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ were ± 0.3 and $\pm 0.000015\%$, $^{87}Rb/^{86}Sr \pm 0.5$, $^{87}Sr/^{86}Sr \pm 0.000025\%$ according to results of multiple standard analyses (external reproducibility). The 2σ errors cited in Table 5 for $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ reflect in-run precision. The blank level was 0.01 ng for Sm and 0.05 ng for Nd, 0.05 ng for Rb and 0.2 ng for Sr. The data obtained for the BCR-1 standard are: [Sr] = 335.8 ppm, [Rb] = 47.16 ppm, [Sm] = 6.487 ppm, [Nd] = 28.45 ppm, $^{87}Sr/^{86}Sr = 0.705053 \pm 11$, $^{87}Rb/^{86}Sr = 0.40615$, $^{143}Nd/^{144}Nd = 0.512663 \pm 9$, $^{147}Sm/^{144}Nd = 0.13829$. Some samples were analysed for Sr- and Nd-isotope ratios by the radiogenic isotope lab of Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany. The error estimate for $^{147}Sm/^{144}Nd$ is $\pm 0.01\%$ (2σ), for $^{147}Sm/^{144}Nd \pm 1\%$. La Jolla $^{143}Nd/^{144}Nd$ standard: 0.511844 ± 15 (2σ).

Reconnaissance oxygen and carbon isotope analysis on ten whole-rock samples was done by the stable isotope lab of the University of Göttingen (Prof. Hoefs). The sample powder was treated with 100% phosphoric acid, and the liberated CO_2 was measured with a Finnigan MAT 251 mass spectrometer. The results of the oxygen and carbon isotope analyses are given in the usual permil deviation relative to SMOW and PDB, respectively (Table 6). The reproducibility of both δ values is better than $\pm 0.2\%_o$. Potassium–argon dating of two dark mica concentrates was by the isotope lab of Bundesanstalt für Geowissenschaften und Rohstoffe (Table 1). Argon was measured by isotope dilution with a mean standard deviation of 0.75% (2σ). Optical petrography was accompanied by qualitative electron microprobe analysis by a Cameca SX 100 at Technical University of Clausthal.

Petrology

In the following section we will give an overview of the petrography and geochemistry of the major igneous rocks of the Ayopaya alkaline province, with focus on the Cerro Sapo complex and the Chiaracke intrusion.

Cerro Sapo alkaline complex

The Cerro Sapo intrusion (Fig. 2) consists predominantly of biotite-clinopyroxene-nepheline syenite/foyaite and sodalite–orthoclase foyaite/syenite with minor ijolite. The mineral assemblage comprises microperthitic orthoclase, nepheline, sodalite, clinopyroxene, plagioclase, biotite, barkevikite, natrolite, cancrinite and apatite. The clinopyroxene is diopside with aegirine–augite rims. Sodalite is ubiquitous and represents the latest magmatic mineral phase. Sodalite is a rare foid-mineral that is characterised by unusually high Na_2O (up to

Table 4 Geochemical data of kimberlite and the melilitic to nephelinitic to basanitic rocks of Ayopaya

	Kimberlite	Melilititic nephelinitic breccias and diatremes										Melilititic nephelinitic basanitic dykes								
	I1	I6a-M-1	I6c-M-1	I6e-M-1	I6 g-M-1	I6 h-M-1	I6i-M-1	I 101 a	I 101 c	I 70e	I 111b	I10	I36	I47	I89	I112	I116	I119	I134b	I136
SiO_2 (wt %)	29.8	35.7	38.5	42.9	37.1	34.3	42.6	30.8	39.7	36.6	33.6	40.0	41.0	39.3	43.5	31.9	44.5	32.5	43.5	37.6
TiO_2	2.17	2.03	1.60	1.49	2.34	1.94	1.68	1.84	1.83	2.00	2.00	2.51	2.42	2.08	2.17	2.37	2.01	2.79	2.28	2.31
Al_2O_3	3.40	9.31	11.4	12.6	10.9	8.89	12.9	7.42	11.0	9.20	8.52	13.6	12.6	11.6	13.8	8.40	13.1	9.50	15.6	11.7
ΣFe_2O_3	10.6	9.33	8.83	8.97	9.48	9.04	8.78	9.90	9.65	10.2	12.6	11.0	11.7	10.3	9.70	10.7	10.8	12.8	10.5	10.2
MnO	0.13	0.28	0.47	0.35	0.24	0.32	0.22	0.26	0.41	0.28	0.50	0.19	0.17	0.26	0.16	0.23	0.16	0.24	0.16	0.19
MgO	22.2	13.7	9.69	8.95	10.6	13.2	9.69	13.5	11.2	13.8	12.3	8.26	9.46	9.74	8.56	12.9	9.45	14.0	4.94	9.14
CaO	10.0	10.6	10.8	9.21	12.9	10.3	8.47	10.1	10.1	13.4	16.8	11.3	10.7	11.2	9.30	17.8	10.1	15.9	7.60	12.0
Na_2O	0.09	3.90	3.78	6.35	4.65	3.28	5.99	2.69	3.32	4.30	1.57	2.91	2.74	2.95	4.03	2.99	2.67	3.43	4.64	2.75
K_2O	0.02	2.98	3.23	2.34	2.54	3.77	3.38	3.02	3.55	1.89	3.22	1.75	2.11	1.11	0.69	1.90	2.10	1.63	1.73	1.52
P_2O_5	0.48	0.67	0.68	0.26	0.74	0.67	0.60	1.13	1.08	1.20	0.27	0.98	0.91	0.88	1.07	0.79	0.58	0.39	0.90	0.87
CO_2	15.7	8.19	8.55	3.82	5.39	11.3	2.47	18.4	6.05	4.11	5.96	3.22	3.00	6.89	1.53	5.63	1.25	2.42	4.91	9.70
Cl	1.47	0.195	0.117	0.671	0.440	0.107	0.607	NA	NA	0.249	NA	0.009	0.009	NA	NA	NA	NA	NA	NA	NA
F	0.079	0.384	0.413	0.182	0.315	0.696	0.158	1.07	0.466	2.30	NA	0.089	0.066	NA	NA	NA	NA	NA	NA	NA
H_2O	3.35	1.84	0.97	0.51	1.29	1.45	0.72	0.42	0.79	NA	1.66	3.36	2.43	2.22	4.27	3.21	1.81	3.34	2.05	0.82
Total	99.5	99.1	99.0	98.6	98.9	99.2	98.3	100.5	99.1	99.5	99.0	99.2	99.3	98.5	98.8	98.8	98.5	99.0	98.8	98.8
Sc (ppm)	16	25	19	21	29	23	23	37.0	23.0	16.5	23.3	21	21	26.0	16.7	20.5	25.2	20.2	14.9	24.9
V	166	202	164	195	231	190	199	377	221	251	168	230	206	214	190	183	195	185	161	514
Cr	1,481	936	596	504	770	897	641	678	792	590	623	192	310	454	209	468	441	528	68	514
Co	79	58	43	47	47	54	42	58	49	36	56	46	56	41	41	57	49	62	35	45
Ni	1,058	411	288	270	259	404	277	386	293	301	267	121	150	177	131	273	157	287	39	133
Cu	43	60	35	127	116	55	56	40	39	43	17	44	35	48	24	45	31	9	30	41
Zn	78	181	666	251	135	213	145	268	335	150	286	102	99	93	112	162	106	126	87	73
Ga	11	11	13	18	14	14	16	14	12	12	10	18	18	11	19	12	12	12	15	12
As	<2	21	64	21	18	81	49	16	61	13	4	2	3	<2	4	2	6	6	<2	<2
Rb	<5	206	220	158	140	238	165	198	190	110	79.3	99	93	51	51	65	83	51	59	84
Sr	373	1,487	1,586	992	1,986	1,769	1,546	970	1,640	1,492	2,150	1,078	819	864	872	2,781	1,004	2,028	890	854
Y	14	50	55	44	51	63	53	48	47	35	79	23	24	26	25	42	23	36	23	26
Zr	179	180	215	196	222	163	204	119	202	193	170	221	210	155	168	175	169	165	213	203
Nb	95	128	171	186	122	160	145	199	153	139	588	112	104	100	104	302	85	256	105	144
Mo	9	21	27	27	38	25	16	10	12	12	<5	13	18	<5	19	<5	12	12	<5	<5
Sn	<2	12	27	<2	7	9	92	5	12	13	<5	<5	4	<5	4	2	6	6	<5	<5
Cs	<5	15.9	24.8	12.6	10.5	17.5	12.0	13.5	23.0	6.0	5.2	18	10	17.7	82.3	1.42	21.5	1.70	15.7	15.7
Ba	310	2,101	1,586	993	2,130	2,879	1,886	1,928	2,040	1,623	2,316	980	666	1,047	914	632	800	537	753	1,058
La	98.3	205	222	252	195	259	238	9.95	145	176	319	61.2	49.3	51.4	51.3	205	40.8	178	49.2	69.1
Ce	162	400	360	252	195	259	238	26.6	240	289	643	114	90.7	92.7	94.8	364	76.8	335	89.5	124
Pr	19.7	44.9	36.1	27.1	18.4	26.9	24.1	2.73	24.4	29.5	73.9	13.1	10.5	10.8	11.1	40.0	9.14	37.6	10.4	14.1
Nd	77.9	138	111	86.8	61.0	85.4	77.6	11.1	79.5	95.0	246	50.0	41.3	40.1	40.9	136	34.6	127	36.8	49.8
Sm	13.1	18.3	16.7	14.0	10.6	14.0	12.4	3.69	12.7	13.3	35.7	9.23	7.91	7.44	7.85	19.9	6.67	19.2	6.85	8.63
Eu	3.52	4.92	4.86	3.95	3.32	4.07	3.53	1.64	3.68	3.77	10.4	2.78	2.48	2.43	2.49	5.84	2.10	5.60	2.20	2.62
Gd	9.66	13.1	13.4	10.9	9.66	11.6	11.0	5.69	10.3	9.85	26.2	8.05	7.12	6.79	6.95	14.9	6.05	14.0	6.15	7.31
Tb	1.08	1.68	1.81	1.50	1.33	1.65	1.54	1.00	1.38	1.23	3.36	1.06	0.94	0.92	0.92	1.87	0.85	1.75	0.83	0.98
Dy	4.56	9.02	9.80	8.34	7.46	9.48	8.69	5.76	7.50	6.37	17.1	5.42	4.81	4.90	4.83	9.38	4.58	8.40	4.39	5.13
Ho	0.64	1.63	1.71	1.54	1.38	1.88	1.64	1.07	1.43	1.13	2.91	0.95	0.82	0.92	0.84	1.57	0.82	1.39	0.78	0.91
Er	1.43	4.31	4.64	4.20	3.97	5.37	4.48	2.89	3.74	2.92	7.12	2.55	2.09	2.34	2.12	3.63	2.05	3.13	2.08	2.38
Tm	0.15	0.61	0.63	0.64	0.53	0.78	0.62	0.42	0.55	0.40	0.88	0.32	0.25	0.32	0.30	0.42	0.28	0.37	0.28	0.32
Yb	0.76	3.59	3.93	4.31	2.96	4.68	3.58	2.82	3.43	2.48	4.85	1.98	1.51	2.02	1.72	2.18	1.66	2.00	1.78	1.90
Lu	0.10	0.48	0.54	0.69	0.40	0.63	0.46	0.44	0.49	0.38	0.65	0.31	0.23	0.29	0.25	0.28	1.66	0.27	0.27	0.28

Table 4 (Contd.)

	Kimberlite	Melilititic nephelinitic breccias and diatremes										Melilititic nephelinitic basanitic dykes								
	I1	I6a-M-1	I6c-M-1	I6e-M-1	I6 g-M-1	I6 h-M-1	I6i-M-1	I 101 a	I 101 c	I 70e	I 111b	I10	I36	I47	I89	I112	I116	I119	I134b	I136
Pb	4.20	20.4	111	44.6	31.6	26.1	35.8	43.5	174	12.6	4.12	<4	<4	10.3	5.52	6.56	4.10	4.26	4.99	13.5
Th	12	35.2	51.5	22.7	2.81	15.6	7.83	3.50	23.2	22.0	36.0	<5	<5	7.76	8.45	11.5	6.29	13.9	8.20	9.26
U	6	1.56	2.08	1.12	2.87	2.26	3.07	0.70	2.02	2.40	3.39	8	4	1.80	2.07	4.54	1.56	3.52	1.77	2.25
(Na + K)/Al	0.05	1.09	0.91	1.00	0.96	1.18	1.06	1.15	0.93	0.98	0.85	0.50	0.57	0.51	0.49	0.85	0.54	0.78	0.59	0.53
Mg#	0.79	0.72	0.66	0.64	0.67	0.72	0.66	0.71	0.67	0.71	0.64	0.57	0.59	0.63	0.61	0.68	0.61	0.66	0.46	0.61

Samples I6a to I101c are from the diatreme of the Laguna Khoallaqui

NA not analysed

Table 5 Sm–Nd and Rb–Sr isotope data for bulk-rock samples from the Ayopaya alkaline province

Sample	Rock	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$(^{143}Nd/^{144}Nd)_i$	ε_{NdT}	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$(^{87}Sr/^{86}Sr)_i$
Cerro Sapo complex												
I 28	Nepheline syenite	9.6	62.5	0.093	0.512734 ± 5	0.512673	3.1	198	1,306	0.437	0.703946 ± 5	0.703325
I 29	Ijolite	[a]11.0	[a]66.6	0.100	0.512727 ± 15	0.512662	2.9	[a]120	[a]1,409	0.247	0.703887 ± 18	0.703466
I 30	Foyaite	[a]6.5	[a]40.6	0.098	0.512753 ± 17	0.512689	3.5	[a]203	[a]1,519	0.360	0.703821 ± 17	0.703207
I 22	Ferrocarbonatite	[a]183	[a]752	0.147	0.512781 ± 11	0.512685	3.4	[a]50.0	[a]4,870	0.012	0.705351 ± 31	0.705331
I53a	Calciocarbonatite	88.8	640	0.090	0.512782 ± 5	0.512723	4.1	12.1	14,500	0.002	0.703441 ± 6	0.703439
Cerro San Cristobal												
I 34	Hornblende syenite	[a]7.2	45.2	0.097	0.512647 ± 12	0.512584	1.4	207	679	0.883	0.705639 ± 33	0.704133
Cerro Quenamari												
I 46	Nepheline syenite	[a]9.9	[a]51.7	0.116	0.512736 ± 14	0.512660	2.9	89.5	1,127	0.230	0.704558 ± 17	0.704166
Chiaracke complex												
I74	Magnesiocarbonatite	182	1,371	0.080	0.512785 ± 8	0.512732	4.3	55.0	6,300	0.025	0.703930 ± 4	0.703894
I77	Magnesiocarbonatite	109	807	0.082	0.512809 ± 9	0.512756	4.9	20.0	790	0.073	0.704787 ± 5	0.704684
I78	Magnesiocarbonatite	102	852	0.072	0.512812 ± 8	0.512765	4.8	2.0	824	0.007	0.704542 ± 23	0.704533
I79	Magnesiocarbonatite	129	1,075	0.073	0.512793 ± 7	0.512746	4.6	5.0	1,770	0.008	0.706211 ± 8	0.706199
I81	Magnesiocarbonatite	[a]253	[a]2,144	0.071	0.512831 ± 5	0.512784	5.4	[a]0.7	[a]530	0.004	0.703473 ± 22	0.703468
Dykes and diatremes (Ayopaya)												
I 36	Nephelinite	[a]8.9	[a]46.0	0.116	0.512796 ± 12	0.512720	4.1	[a]79.4	[a]1,504	0.153	0.704651 ± 20	0.704391
I 6a	Melilititic diatreme	[a]16.8	[a]101	0.101	0.512697 ± 11	0.512631	2.3	[a]213	[a]1,629	0.378	0.704362 ± 25	0.703718
AY22	Kimberlite	[a]14.3	[a]83.5	0.104	0.512637 ± 6	0.512569	1.2	[a]2.8	[a]443	0.018	0.705398 ± 32	0.705373
I1	Kimberlite	13.1	77.9	0.102	0.512683 ± 6	0.512616	2.1	22.0	373	0.170	0.707137 ± 4	0.706853

Initial Nd and Sr isotope data are recalculated to $t = 100$ Ma

[a]Data have been measured by isotope dilution, all others by ICP-MS

Table 6 Carbon and oxygen isotopic composition of carbonatite samples from Ayopaya

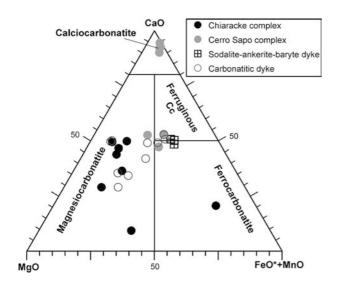| Sample	Rock	$\delta^{13}C_{PDB}$	$\delta^{18}O_{SMOW}$
I5	Ferrocarbonatite	−4.68	12.6
I22	Ferrocarbonatite	−4.72	14.0
I40	Calciocarbonatite	−9.18	10.9
I62	Calciocarbonatite	−7.67	7.16
I53a	Calciocarbonatite	−8.64	10.3
I53b	Calciocarbonatite	−8.08	11.0
I70a	Ferrocarbonatite	−5.37	14.3
I78	Magnesiocarbonatite	−4.94	11.9
I81	Magnesiocarbonatite	−5.70	12.3
I82	Magnesiocarbonatite	−6.16	12.1

25 wt%) and Cl (up to 5 wt%) contents. The rocks are highly alkaline to peralkaline (Table 2). Most samples have (Na$_2$O-2) > K$_2$O indicating a highly sodic character (Le Bas et al. 1986).

A small calciocarbonatitic intrusive body occurs in the sedimentary host rock north–west of the nepheline-syenitic stock (Fig. 2). The body is accompanied by a network of calciocarbonatitic to ferrocarbonatitic dykes and dykelets and has a surface expression of 300 by 900 m (Balderrama Zàrate 2003). The thickness of the dykes ranges from a few centimetre to several metre. Calciocarbonatitic dykes have also been found inside the syenitic stock. Ahlfeld and Mosebach (1935) found large boulders (up to 10 m) of white carbonatite in the Khori Mayu river in the immediate vicinity of the syenitic stock and described them first as "marbles", later reinterpreted as possible carbonatites (Ahlfeld 1966). The rocks represent nearly pure equigranular anhedral to subhedral calciocarbonatite with smaller patches of ferruginous silicocarbonatites (Fig. 4). Ahlfeld and Mosebach (1935) also reported on abundant purple fluorite layers. The mineral association of these carbonatites comprises predominantly calcite with minor amounts of stron-

tianite, apatite, Sr- and REE-rich hydroxylcarbonates (ancylite group) and fluorcarbonates (synchysite group), baryte, pyrite, sphalerite, amphibole, pyrochlore, diopside, and mica. Small ferrocarbonatitic dykes in the sedimentary host rock are associated with the calciocarbonatite intrusion, and contain synchysite/parisite, minor churchite (Dy-Gd-phosphate), and an exotic Th-rich mineralisation with thorite and thorbastnaesite.

Typical of all calciocarbonatite dykes is the intense narrow layering parallel to the contact planes, which likely represents a fluidal texture (flow banding). The banding is characterised by layers of pyrochlore, strontianite, apatite, fluorite, amphibole and pyrite. Geochemically, the calciocarbonatites (Table 3) are characterised by low silica content (< 2.2 wt% SiO$_2$) and low content of alkalis (< 1 wt% Na$_2$O + K$_2$O). They represent nearly pure carbonate rocks with CaCO$_3$ > 87wt%. The calciocarbonatites show variable degree of REE enrichment and a relatively smooth REE distribution pattern similar to the intrusive silicate rocks of the Cerro Sapo area (Fig. 5). In contrast, the sodalite–ankerite–baryte dyke displays strong enrichment in the MREEs. The calciocarbonatites are strongly enriched in Sr (up to 4 wt%) and Nb (up to 2,000 ppm). The thorium content of a small ferrocarbonatitic dyke (Table 3: I123) reaches 6,400 ppm Th.

The nepheline-syenitic stock and the sedimentary host rock of the Cerro Sapo complex are cross-cut by a NW–SE trending sodalite-ankerite-baryte dyke (Fig. 2). The dyke has a length of more than 3 km and is up to 8 m thick. It consists of large irregular patches or bands of dark-blue sodalite changing rapidly with white-to-yellow ankerite and white baryte. This dyke is currently mined as semi-precious stone and ornamental rock.

The sodalite–ankerite–baryte dyke shows a fascinating textural variety comprising rhythmic layering and

Fig. 4 Carbonatite samples from the Ayopaya alkaline province in the revised classification diagram of Gittins and Harmer (1997); data plotted in molar proportions

Fig. 5 REE distribution patterns for calcio- and magnesiocarbonatite samples from the Cerro Sapo and Chiaracke complexes, respectively, and a representative sample (AY24) from the sodalite–ankerite–baryte dyke at Cerro Sapo. The *grey shaded field* shows the composition of worldwide carbonatite occurrences compiled by Hornig-Kjarsgaard (1998). Normalising values from Evensen et al. (1978). *Inset* (**b**) shows average composition of magnesio- and calciocarbonatite samples compared to the kimberlite dyke (sample I1) and average syenite/foyaite from Ayopaya

fluidal flow textures (e.g. marble cake texture) (Fig. 3). Nearly monomineralic sodalite patches in the dyke have several metres in diameter and are subhedral-granular textured. Some euhedral sodalite crystals reach up to 9 cm in size and can be described as pegmatitic. The dyke shows a very sharp intrusive contact to the magmatic nepheline-syenitic host rocks (Fig. 3). The contact zone in the syenitic host rock is brecciated and displays an intense sodalite-ankerite stockwork, with narrow zones of fenitisation (Fig. 3). Due to the strong textural and compositional heterogeneity the contribution of the main components to the dyke can only be estimated at about 40–45% sodalite, 40–45% ankerite, 10–12% baryte. Siderite, calcite, natrolite, analcime occur in minor amounts. Locally, patches and veinlets of galenite, sphalerite, pyrite and chalcopyrite occur within the dyke. Ahlfeld and Mosebach (1935) also reported native gold in strongly weathered parts. Sodalite-rich parts of the dyke contain micro-crystal nests and veinlets of alkali-feldspar, nepheline, diopside and amphibole.

The ankerite, and sometimes also the sodalite component, contains strontium-, thorium- and REE-rich minerals such as strontianite, Sr-apatite, daqingshanite, REE-bearing strontianite, minerals of the crandallite group (goyazite), hydroxylcarbonates (mckelveyite), and Sr-rich zeolites (bellbergite). The mineral assemblage is reflected by high bulk-rock REE contents (Σ REE up to 0.45 wt%) and up to 2,000 ppm Th. Remarkable is the occurrence of REE-rich Sr-carbonates which contain very high amounts of thorium (1.5–10 wt% ThO_2).

Chiaracke carbonatite intrusion

The Chiaracke intrusion, discovered by Matos (2000), is exposed about 5 km southwest of the Cerro Sapo at 4,100 m a.s.l. over an area of about 1×2 km (Fig. 1). The Chiaracke complex represents a magnesiocarbonatitic intrusion which is accompanied by many small dykes and m-sized lens-shaped bodies (1–3 m wide) of ferro-carbonatitic to silicocarbonatitic composition as well as carbonate-rich phlogopite breccias occurring widespread in the Ordovician sedimentary host rock. The carbonatite body consists of white-brown to brown coloured rocks, often showing an intense dark-brown layering. Secondary hydrothermal veinlets are characterised by purple-coloured fluorite. The mineral association of the Chiaracke intrusion comprises predominantly dolomite (Fig. 4) but also ankerite, magnesite, calcite, fluorite, strontianite, bastnaesite, monazite, apatite, potassic feldspar and magnetite.

Bastnaesite-(Ce) and monazite occur dispersed and on fissures and micro-veinlets in the carbonatite. Monazite veinlets are often associated with apatite and baryte. REE minerals of the crandallite group (florencite–goyazite) occur on veinlets together with baryte and purple-coloured fluorite. The ferrocarbonatitic to silicocarbonatitic dykes and lens-shaped bodies are characterised by small nests and veinlets of feldspar and apatite, and sometimes large mica megacrysts up to several centimetre in size.

The magnesiocarbonatite is characterised by low silica content (mostly < 1 wt% SiO_2) and low alkali content (< 0.25 wt% $Na_2O + K_2O$), and strong enrichment in LREEs (up to 3,800 ppm La, 6,600 ppm Ce, 2,100 ppm Nd, 250 ppm Sm) (Table 3) with steep REE patterns (La/Yb from 580 to 1,500) (Fig. 5). Compared to the calciocarbonatite of the Cerro Sapo the magnesiocarbonatite shows relatively low concentrations of niobium (10–170 ppm Nb), zirconium (mostly below 100 ppm Zr), and sometimes strontium, but higher contents in barium (up to 10 wt% Ba) and thorium (> 200 ppm Th) (Fig. 6).

Melilititic to nephelinitic dykes and diatremes

The ultramafic diatremes in the Khoallaqui (Laguna Khoallaqui) area, about 10 km N of Independencia, were the first targets of diamond exploration in the Ayopaya province. Due to their close textural similarity they have first been interpreted as kimberlitic pipes (Matos 1990). Based on petrography and geochemistry, however, they classify as melilititic to nephelinitic rocks (e.g. Fig. 7) (Lehmann and Schultz 1999).

Melilititic to nephelinitic dykes and diatremes occur widespread in the entire Ayopaya region as pale- to dark-grey fine-grained to aphanitic rocks in the sedimentary host rock. The diatremes have round to elongated shape of 10–100 m in size and are accompanied, respectively cut, by phonolitic to tephritic rocks which occur as late-stage dykes or rims around the diatremes. The diatreme rocks are dark-grey to greenish or brown and have autolithic clasts, pelletal lapilli, xenoliths and a complex suite of mega- and macrocrysts in a very heterogeneous groundmass. The
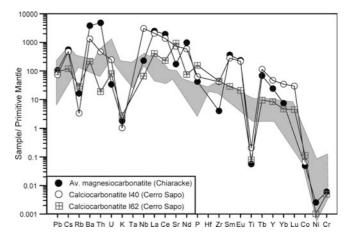

Fig. 6 Average trace-element abundances of magnesiocarbonatite from Chiaracke compared with calciocarbonatite from the Cerro Sapo, normalised to primitive mantle (after McDonough and Sun 1995). *Grey shaded field* is composition of nepheline syenite/foyaite
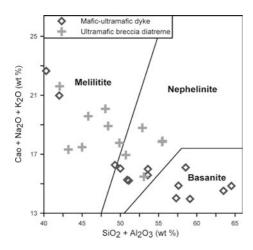
Fig. 7 Ultramafic breccias and dykes from Ayopaya in the combined oxides diagram for discrimination between melilitite, nephelinite and basanite after Le Bas (1989)

mega- and macrocryst suite consists of different populations of forsteritic olivine and minor amounts of clinopyroxene (augite to diopside) and phlogopite. The olivine population comprises rounded mega- to macrocrysts (Mg# 0.78–0.89) but also skeletal olivine phenocrysts ("hoppers"), including "unusual hoppers" (after Moore and Erlank 1979), i.e. olivine with Mg-rich rims and Fe-rich cores. Further macrocrysts are melanite, nepheline, sodalite, chromite, perovskite, ilmenite, magnetite, pyrite and apatite. Fragments of orthoclase, sodalite and aegirine-augite are probably derived from nepheline syenite. The very heterogeneous groundmass of the dykes and diatremes comprises microlithic phlogopite, serpentine, perovskite, chromite, clinopyroxene, carbonate, apatite and glass. Zeolite pseudomorphs after lath-like melilite microcrystals are visible in some dykes. The pseudomorphs are fluidal-textured and show the typical peg-structure. They indicate a primary melilite content of up to 40%. Primary carbonate occurs as groundmass mineral as well as carbonatitic patches and lenses of m-size in the diatremes.

The predominantly melilititic to nephelinitic character of the dykes and diatremes (Fig. 7) is also indicated by normative larnite contents from 2 to 15% (see Woolley et al. 1996). Compared with kimberlites they are rich in Na_2O and Al_2O_3 and poor in MgO (Mg# between 0.67 and 0.72). Some of the samples can be classified as peralkaline (Table 4). The dykes and diatremes predominantly represent silica-undersaturated rocks with average titanium contents of 2.4 wt% TiO_2.

Besides fragments from the sedimentary and igneous host rocks, the xenolith association of the melilititic to nephelinitic diatremes and dykes also comprises samples from the basement (gneisses) and upper mantle (lherzolitic peridotite, wehrlite, clinopyroxenite). The clinopyroxenite xenoliths are 0.5–8 cm in diameter and are rounded to weakly angular. The texture of the xenoliths is variable ranging from granular to porphyroclastic. They consist of different types of clinopyroxene,

together with amphibole, phlogopite, apatite, carbonate, titanomagnetite, melanite, sphene, and rare feldspar. The anhedral to subhedral pyroxenes are pale-green to dark-green and sometimes irregularly patchy zoned. Apatite occurs in veinlets but also intergranular between clinopyroxene crystals. Large euhedral apatite laths (> 1 cm), crosscutting the crystal faces of clinopyroxene, are probably of secondary origin.

Kimberlitic dyke

About 4 km NE of Independencia, a strongly weathered, dark-grey, carbonate-serpentine-rich kimberlitic dyke occurs in Ordovician shale (Fig. 1) at nearly 3,000 m a.s.l. The steeply dipping dyke has a length of about 300 m and a thickness of a few metres. The dyke has a porphyritic texture with white to light-greenish, rounded phenocrysts (0.2–0.6 cm in size) and hypidiomorphic dark phenocrysts (1–3 mm in size) set in a fine-grained dark-grey to greenish-grey groundmass. The phenocrysts constitute 25–30% of the rock. They are completely replaced by carbonate (white) and serpentine (dark) in variable proportions, with chrysotile along cleavage planes. Relics of phlogopite (up to several millimetre large) are mostly replaced by brown hydromica (Fig. 8). The groundmass consists of calcite pseudomorphs of olivine (?) and serpentine. Accessory mineral phases of the groundmass are chromite, perovskite, monazite, apatite, magnesite, magnetite, monticellite, pyrite and rutile.

In spite of advanced weathering and alteration, the geochemical features of this rock clearly indicate a kimberlitic composition (Table 4). This rock has the highest MgO content of all silicate rocks of the Ayopaya region with more than 22 wt% MgO and a high Mg# number of 0.79 (Table 4). Archetype kimberlites are characterised by MgO values of 25–30 wt% (Mitchell 1986), and the slightly lower value of the Ayopaya samples may be caused by the distinctive carbonatisation. High CO_2-contents (up to 16 wt%) are also typical of hypabyssal kimberlites (Clement 1982). The high content of chromium (1481 ppm Cr) and nickel (1058 ppm Ni) and the steep REE distribution pattern are diagnostic for kimberlite (Fig. 9). Particularly the strong enrichment of light REE, and the strong REE fractionation (La/Yb = 103) exclude a cumulate origin. The trace element pattern of the kimberlite is very similar to that of average Group I kimberlite (Fig. 9).

Kimberlitic dykes typically occur in the roots of kimberlite pipes, where they form vertically dipping tabular bodies of 1–3 m thickness (maximum 10 m) (Clement et al. 1973; Mitchell 1986). Given the relatively deep exposure level of the dyke at 3,000 m a.s.l., the diatreme-facies of the kimberlite system is likely to be eroded, whereas the melilititic diatremes at Laguna Khoallaqui, which occur at an altitude of about 4,000 m a.s.l., are still preserved.
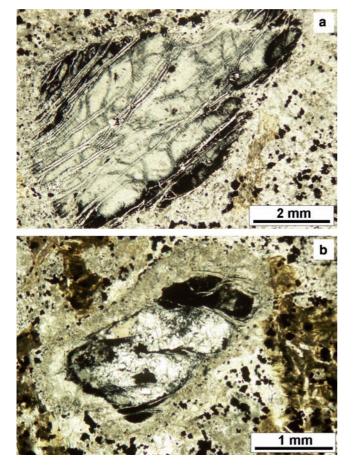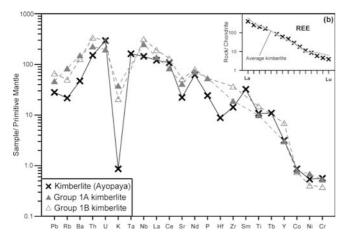
Fig. 8 a Serpentinised phenocryst of olivine with chrysotile on cleavage planes and rim of opaque minerals. **b** Pseudomorphic calcite and serpentine after anhedral-rounded olivine xenocryst in fine-grained carbonate-serpentine groundmass with opaque phases (chromite, magnetite)

Fig. 9 Trace-element data of the kimberlite dyke compared with average Group IA and Group IB South African kimberlites (after Smith et al. 1985). Potassium depletion of the kimberlite sample is due to alteration. Data normalised against primitive mantle (after McDonough and Sun 1995). **b** Comparison of the REE pattern of the kimberlite sample from Ayopaya with average kimberlite (*grey line*) according to Bergman (1987) (chondrite values from Evensen 1978)

Discussion

Nd and Sr isotope constraints on the origin of the alkaline rock spectrum

Rb–Sr and Sm–Nd isotope data are listed in Table 5 and plotted in Fig. 10 for $t = 100$ Ma. The alkaline rock suite from Ayopaya (carbonatite, nepheline syenite, foyaite, melilitite, nephelinite, kimberlite) shows positive ε_{Nd} values of 1.4–5.4 indicating a depleted mantle source. The Chiaracke magnesiocarbonatite has high to very high ε_{Nd} values together with relatively high $^{87}Sr/^{86}Sr$ ratios. The $^{87}Sr/^{86}Sr$ range of the magnesiocarbonatite, particularly the most radiogenic value ($^{87}Sr/^{86}Sr = 0.70620$), can be attributed to hydrothermal overprint. Calcite veinlets are widespread both within and around the Chiaracke complex.

The two carbonate–phlogopite kimberlite samples have initial $^{143}Nd/^{144}Nd$ ratios (ε_{Nd} 1.2 to 2.1) corresponding to group I kimberlites of South Africa. Their radiogenic Sr isotope ratios ($^{87}Sr/^{86}Sr$ 0.70537–0.70685) must be attributed to post-magmatic fluid overprint.

The syenitic sequence (nepheline syenite, foyaite, ijolite, hornblende syenite), a melilititic diatreme rock and the calciocarbonatite samples plot exclusively in the depleted mantle sector and form an array to progressively higher $^{87}Sr/^{86}Sr$ ratios and lower ε_{Nd} values (Fig. 10). Their Nd isotope range is remarkably narrow, given the wide petrographic rock spectrum and suggests a close genetic relationship. Like in other alkaline rock provinces (Harmer and Gittins 1998; Bizimis et al. 2003) the carbonatites have the most depleted isotopic compositions. The isotopic trend for the silicate rocks is not correlated to degree of magmatic fractionation. Major crustal contamination of the Sr and Nd isotope systems is unlikely for most of the Ayopaya samples because of their elevated strontium (e.g. > 1,300 ppm Sr at the Cerro Sapo complex) and neodymium concentrations (> 40 ppm Nd). The linear array stretches in between the two major mantle reservoirs HIMU and EM I (as defined by Zindler and Hart 1986) (Fig. 10). Similar linear trends can also be observed for most alkaline rocks in the East African rifts, e.g. Oldoinyo Lengai (Bell and Simonetti 1996) (Fig. 10). This trend either reflects mixing of two mantle components in a heterogeneous mantle plume (Bell and Tilton 2001), or mixing between a metasomatised EM-I type lithosphere and a plume-derived asthenospheric HIMU component (Bell and Simonetti 1996; Bizimis et al. 2003).

The composition of the most depleted magnesiocarbonatite sample from Ayopaya (ε_{Nd} 5.4, $^{87}Sr/^{86}Sr = 0.70347$) is close to the HIMU reservoir (Fig. 10). Most magnesiocarbonatite samples plot in the range of plume-related oceanic island basalts such as Trindade Island (Siebel et al. 2000) (Fig. 1). These observations indicate that the Chiaracke magnesiocarbonatite represents an asthenospheric mantle component. The silicate rocks, but also the calciocarbonatites of the Ayopaya province
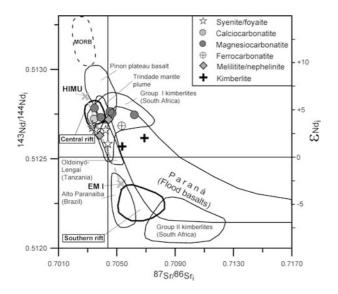
Fig. 10 Sr–Nd-isotope diagram for rocks from the Ayopaya alkaline province (recalculated to $t = 100$ Ma). Comparison with igneous rocks of similar age from South America and related rock types worldwide. Group I and II kimberlites (Kramers et al. 1981; Smith 1983), Oldoinyo Lengai (Bell and Dawson 1995), kamafugites and lamproites from Alto Paranaiba, SE Brazil (Gibson et al. 1995), Paraná flood basalts (Hawkesworth et al. 1986; Petrini et al. 1987), MORB (White and Hofmann 1982; O'Nions et al. 1977), HIMU and EM I (Hart et al. 1992), Central rift and Southern rift in Argentina (Lucassen et al. 2002). CHUR and Bulk Earth are recalculated from present-day values of 0.512638 and 0.7045, respectively, to 100 Ma

($\varepsilon_{Nd} \leq 4.1$), seem to represent a slightly different mantle source with a stronger contribution of an enriched component which may be the lithospheric mantle (EM-I like).

Similar to the alkaline complexes of East Africa, the Ayopaya province is part of a continental rift system (Fig. 1b). Samples of nephelinite and basanite from the prolongation of the Bolivian rift to northern Argentina at 25°S ("Central Rift" in Fig. 10, according to Lucassen et al. 2002) show the same depleted isotope signature as the most primitive samples from Ayopaya. The isotopic pattern of the rift-related Mesozoic rock suite is different from the isotopic composition of the subcratonic Mesozoic alkaline rocks from the Brazilian Shield (Fig. 10). The Brazilian samples from the Alto Paranaiba igneous province result from interaction of a mantle plume (e.g. Trindade hot spot, Fig. 1b) with the Archaean to Proterozoic lithospheric mantle (e.g. Gibson et al. 1995), whereas the rift-related Central Andean alkaline rocks reflect the non-cratonic Central Andean lithosphere as also seen in their Late Proterozoic to Palaeozoic model ages (Lucassen et al. 2002).

Most East African alkaline complexes show isotopic similarities between carbonatites and associated primitive silicate rocks (e.g. melilitites or olivine nephelinites), whereas the evolved silicate rock types show distinctly enriched isotopic compositions. This isotopic difference suggests that the carbonatites and the associated evolved silicate magmas developed as discrete "primary" melts

from the mantle (Harmer and Gittins 1998). In contrast, the isotopic similarity of carbonatites and evolved intrusive silicate rocks (foyaite, nepheline syenite) in the Cerro Sapo complex may indicate a largely mutual mantle source and differentiation by late-stage crustal processes, e.g. liquid immiscibility.

Stable isotope data

The carbon and oxygen isotopic compositions of carbonatite samples from the Ayopaya province are given in Table 6 and plotted in Fig. 11. The data are presented as δ^{13} C vs. PDB and δ^{18} O vs. SMOW. The δ^{13} C range of the magnesiocarbonatite samples from the Chiaracke intrusion and the ferrocarbonatite samples (−4.9 to −6.2‰) corresponds to the primary igneous carbonatite field (Hoefs 1987), and the mantle field (Nelson et al. 1988; Deines 1989) (Fig. 11). The enriched δ^{18}O values of these samples could be attributed to alteration processes and secondary isotopic exchange (Deines 1989; Keller and Hoefs 1995), e.g. weathering, and is similar to those of Mesozoic carbonatites from Brazil (Santos and Clayton 1995).

The calciocarbonatite samples from Ayopaya show an unusual trend of depletion in $\delta^{13}C_{PDB}$ (−7.7 to −9.2‰) with increasing $\delta^{18}O_{SMOW}$ (7.2–11.0‰), which correlates with degree of REE enrichment, and may be related to late-stage magmatic processes such as carbonate fractionation. Similar trends of ^{13}C depletion have been reported from carbonatitic tuffs and lavas,

Fig. 11 Stable isotope composition of carbonatite samples from the Ayopaya alkaline province. The magnesio- and ferrocarbonatites have similar ranges in oxygen and carbon isotope composition, while the calciocarbonatites from the Cerro Sapo complex are characterised by unusually low δ^{13}C. Reference fields for Brazilian carbonatites are from Santos and Clayton (1995); carbonatitic tuff and lava is represented by Kaiserstuhl (Hay and O'Neil 1983) and Oldoinyo Lengai samples (Keller and Hoefs 1995). The compositional field for recycled crustal carbon is defined by carbonatites from Kerguelan Islands (Ray et al. 1999). Mantle and primary carbonatite fields are from Hoefs (1987), Nelson et al. (1988) and Deines (1989)

e.g. from Oldoinyo Lengai, Tanzania, and Kaiserstuhl, Germany (Fig. 11). The isotopic patterns of these rocks are attributed to secondary isotopic exchange by low-temperature alteration/recrystallisation, due to the instability of their natrocarbonates (Hay and O'Neil 1983; Keller and Hoefs 1995). Depletion in ^{13}C can also result from isotopic fractionation between calcite and degassing CO_2 (Suwa et al. 1975; Deines 1989), e.g. partitioning of heavy carbon into CO_2 gas during hydrothermal exchange with CO_2-rich fluids (Chacko et al. 1991).

The calciocarbonatite and magnesiocarbonatite samples have distinctly different $\delta^{13}C$ values which cannot entirely be attributed to secondary processes because of their similar postmagmatic history. Instead, these differences probably reflect different magmatic histories (see below).

Carbonatite petrogenesis

The rock spectrum of the Ayopaya province can be regarded as a paradigm for carbonatite petrogenesis with examples of all three extensively debated models for carbonatite petrogenesis, i.e. primary carbonatitic mantle melts, carbonatites by liquid immiscibility from carbonated silicate melt, and carbonatite as product of crystal fractionation (residual liquid from advanced crystallisation).

The Chiaracke magnesiocarbonatite as primary mantle melt

The Chiaracke intrusion shows a number of features suggestive of an origin as a primary carbonatitic mantle melt from a depth of more than 70 km. These are:

Field relationships The 2-km^2-large intrusive body shows no direct association with magmatic silicate rocks, contrary to the Cerro Sapo complex with its calciocarbonatite suite.

Major element composition High magnesium content, i.e. dolomitic composition, and very low SiO_2 content (Fig. 4) correspond to experimentally defined primitive mantle melts (Wallace and Green 1988; and many others).

REE distribution pattern The Chiaracke samples have very steep REE distribution patterns when compared to other carbonatite samples from world-wide localities (Hornig-Kjarsgaard 1998) and to calciocarbonatite from the Cerro Sapo (Fig. 5). Their slope is similar to the kimberlite dyke which is very close to average kimberlite composition (Mitchell 1986) (Fig. 5b). The typical steep REE pattern of kimberlites is commonly attributed to the presence of residual garnet during low-degree partial melting of garnet lherzolite (e.g. Alibert et al. 1983; Ringwood et al. 1992). The magnesiocarbonatites have a REE distribution pattern parallel to the kimberlite but are enriched by a factor of about 10 (Figs. 5b and 9).

Dalton and Presnall (1998) suggested close genetic links between magnesiocarbonatites and kimberlites. A much flatter REE distribution pattern is shown by all other silicate and carbonate rocks from Ayopaya (Fig. 5).

Trace-element distribution pattern Residual garnet in the source of the magnesiocarbonatite is also indicated by the element patterns in Fig. 6. The magnesiocarbonatite shows characteristically low abundances in Ta, Nb, Sr, Zr, HREE and Y. Partition coefficients for garnet/carbonatite melt (Sweeney et al. 1992) indicate that Ti, Zr, Y and the HREEs are strongly partitioned into garnet. The relatively strong depletion in Nb, Ta and HREEs (Fig. 6) represents a very remarkable feature of the magnesiocarbonatites from Chiaracke, also when compared with the average magnesiocarbonatite of Woolley and Kempe (1989). The strong negative titanium anomaly in Fig. 6 results from the low solubility of Ti in carbonatite melts (Sweeney et al. 1992), and the compatible behaviour of titanium with garnet and amphibole. The Chiaracke magnesiocarbonatite also meets the criteria for a primary carbonatitic mantle melt as defined by Rudnick et al. (1993), i.e. high La/Yb (>500), very low Ti/Eu (<5) and high Ca/Al (60–790).

Neodymium isotope composition The magnesiocarbonatite samples show the highest initial ϵ_{Nd} values (4.8–5.4) of all rocks from the Ayopaya region. These values are high even when compared with the Cretaceous carbonatites of the East African rift systems which are suggested to have a plume source (Bell and Tilton 2001).

The calciocarbonatites of the Cerro Sapo complex as a result of liquid immiscibility

The calciocarbonatites of the Cerro Sapo complex can be attributed to liquid immiscibility of a carbonate-saturated parental silicate melt (melilititic to nephelinitic) under crustal pressure (according to the model of Le Bas 1989; Kjarsgaard and Hamilton 1989) and successive crystal fractionation of the carbonatite melt after segregation. Liquid immiscibility as a reasonable model for the generation of the Cerro Sapo alkaline complex is indicated by:

1. There is a close spatial relationship of calciocarbonatite with nepheline-syenitic rocks in the Cerro Sapo complex. A similar situation can also be observed for the other nepheline-syenitic complexes (Cerro San Cristóbal, Cerro Quenamari) of the Ayopaya alkaline province (Fig. 1). At a metre-scale, some melilititic diatremes host small carbonatite lenses.
2. The calciocarbonatites of the Cerro Sapo intrusion are alkali-poor and their high calcic-carbonate content (>85 wt% $CaCO_3$) excludes a primary mantle origin, but indicates late-stage crustal processes, i.e. liquid immiscibility under crustal pressures (Lee and Wyllie 1997).

3. The trace-element distribution is consistent with liquid immiscibility plus subsequent crystal fractionation. Figure 6 shows two stages of calciocarbonatite evolution on the background of nepheline syenite composition. The first stage, as exemplified by sample I62, results in more or less equal amounts of Th, U, Ta, Nb, Zr, Y and middle and heavy rare-earth elements in the silicate and carbonate fraction. On the other hand, there is a pronounced enrichment of strontium, phosphorus and LREEs in the carbonate phase. This situation is in accordance with the experimental results by Hamilton et al. (1989), Jones et al. (1995) and Veksler et al. (1998b) who determined partitioning coefficients for co-existing silicate–carbonate liquids. Crystal fractionation then modifies the composition of the segregated carbonate liquid (second stage; sample I40) as portrayed by variable degree of REE, Th, Ba and Nb enrichment in accordance with the incompatible behaviour of these elements in a low-pressure carbonate melt-calcite system (Kjarsgaard and Hamilton 1989). The REE patterns of the calciocarbonatite samples are similar to those of the intrusive silicate rocks of the Cerro Sapo complex (average syenite/foyaite in Fig. 5b). The difference is in the degree of total REE enrichment and a slightly stronger LREE/HREE fractionation of the carbonatites.

4. A close genetic relationship between calciocarbonatites and syenites/foyaites of the Cerro Sapo complex is also indicated by their similar Nd–Sr isotopic composition (see above).

The sodalite-ankerite-baryte dyke of the
Cerro Sapo-complex as the result of extreme crystal
fractionation of a carbonated silicate melt

The sodalite-ankerite-baryte dyke of the Cerro Sapo complex represents an exotic and so far unique hybrid carbonate–silicate rock (Table 3) with very variable contents of the three main mineral components. The narrow rhythmic sodalite–ankerite layering and fluidal textures (Fig. 3) of the dyke suggest crystallisation from a silicate-rich carbonatitic melt system.

A genetic relationship between the sodalite-ankerite-baryte dyke and the intrusive silicate stock of the Cerro Sapo complex appears likely in view of the ubiquitous occurrence of sodalite in both rocks and their spatial association. Sodalite clearly represents the latest magmatic solidus phase of the nepheline-syenitic rocks. Inclusions of carbonate microcrysts in late-stage sodalite crystals of some foyaites indicate carbonate saturation of the late-stage residual magma. Additionally to the high carbonate content the occurrence of sodalite documents a strong enrichment in sodium and chlorine of the residual melt (sodalite has up to 24 wt% Na_2O and 5 wt% Cl, Table 2). The parental magma was possibly pre-enriched in alkalis (especially Na) due to the prior separation of an immiscible calciocarbonatite liquid

(Kjarsgaard and Hamilton 1989). High magmatic barium contents like those of the sodalite-ankerite-baryte dyke (maxiumum 10–15 wt% BaO) have also been reported from other carbonatite occurrences, e.g. Mountain Pass, USA, and have been experimentally reproduced (Jones and Wyllie 1983; Mariano 1989).

Radiogenic as well as stable isotope data of the dyke indicate a mantle origin of the carbonate component of the dyke. The ε_{Nd}-value of the ferrocarbonatite-component of the dyke (I22 in Table 5, ε_{Nd} 3.4) is well in the range of the other samples from the Cerro Sapo complex (ε_{Nd} 2.9–3.5) indicating a common depleted mantle source. The mantle origin of the carbonate component of the dyke is also confirmed by a $\delta^{13}C$-value of −4.7 ‰ (Table 6, Fig. 11).

The sodalite-ankerite-baryte dyke may be interpreted to represent the highly fractionated, fluid- and carbonate-rich, peralkaline residual melt or "flotation cumulate" (Ussing 1912; Markl et al. 2001) of the nepheline syenitic intrusion of the Cerro Sapo complex. However, the extreme enrichment in sodium and chlorine could also be understood as a result of exsolution and condensation of a H_2O–CO_2-rich fluid from a carbonated silicate melt, as recently suggested for the Oldoinyo Lengai natrocarbonatite lava flows by Nielsen and Veksler (2002).

Cretaceous natrocarbonatite volcanism in the Ayopaya-
province? Similarities to Oldoinyo Lengai, Tanzania

The sodalite-ankerite-baryte dyke of the Cerro Sapo complex has many geochemical and petrological features in common with the natrocarbonatite lavas of Oldoinyo Lengai in Tanzania. The intrusive Cerro Sapo complex as well as the Oldoinyo Lengai volcano occur in a continental rift environment and are characterised by a similar alkaline assemblage comprising nephelinite, phonolite, nepheline syenite, ijolite, soevite (Dawson 1962; Dawson et al. 1995; Bell and Keller 1995).

The natrocarbonatites of Oldoinyo Lengai and the sodalite–ankerite–baryte dyke of the Cerro Sapo complex are unique in their unusual mineralogical and geochemical composition. Despite distinct differences in their mineral paragenesis they show an intriguing similarity in their characteristic element signatures. Both occurrences reflect late magmatic, fluid-rich systems which can be attributed to carbonate-rich alkaline silicate magmatism and which are characterised by unusual enrichment in Na, Cl, Ba, Sr, F, Br (for the sodalite–ankerite–baryte-dyke see Table 3, for Oldoinyo Lengai see Bell and Keller 1995). The carbonatite lavas predominately consist of the two natrocarbonates gregoryite (Na_2, K_2, Ca, Sr, Ba)CO_3 and nyerereite (Na, K)$_2$(Ca, Sr, Ba)(CO_3)$_2$, sylvine and fluorite (Dawson 1962; Keller and Krafft 1990; Dawson et al. 1995). The solidus of the natrocarbonate melt is reached at < 635 °C at 1–2 kbar (Petibon et al. 1998), or 650 °C at 1 kbar, respectively (Cooper et al. 1975). At pT-conditions higher than the natrocarbonate solidus a

silicate-bearing (natro)carbonatitic melt (> 5 wt% SiO_2 according to Petibon et al. 1998) will first precipitate alkali-rich silicate minerals such as nepheline, combeite, vishnevite, coexisting with carbonate melt (e.g. Kjarsgaard et al. 1995; Petibon et al. 1998).

The textures of the sodalite-ankerite-baryte dyke (Fig. 3) indicate concomitant precipitation of carbonate and silicate phases, and the sodalite-ankerite-baryte dyke of the Cerro Sapo complex can possibly be interpreted as the intrusive equivalent of the recent natrocarbonatite lavas from Oldoinyo Lengai. The petrogenesis of these natrocarbonatites (liquid immiscibility vs. "expulsion of a cognate mobile, alkaline, CO_2-rich fluid condensate") is still much debated (e.g. Nielsen and Veksler 2002).

Conclusions

The Ayopaya alkaline province is the petrologically most exotic expression of large-scale Mesozoic continental rifting along the western South American continent. This situation is similar to the still ongoing rifting in eastern Africa. However, the intracontinental rift evolution of South America represents failed rifts on an active convergent margin, whereas the East African rift magmatism is attributed to mantle plume activity. The Central Andean rift is probably related to plate reorganization in the Pacific region, i.e. a change in subduction from southeastward to northeastward with concomitant crustal attenuation at 80–120 Ma (Jaillard et al. 2000; Sempere et al. 2002).

Neodymium–strontium isotopes indicate mixing between an isotopically depleted asthenospheric mantle and a more enriched mantle component. The asthenospheric mantle is reflected by the magnesiocarbonatite intrusion of Chiaracke which is believed to derive from primary mantle melts (from depth > 70 km) that formed by low-degree partial melting of carbonated peridotite (garnet lherzolite). The survival of magnesiocarbonatite melt on ascent to shallow levels requires metasomatically prepared channelways of wehrlitic to clinopyroxenitic composition (Harmer and Gittins 1997; Wyllie and Lee 1998). Xenoliths of wehrlite and clinopyroxenite occur in ultramafic dykes and diatremes from Ayopaya, but also in other parts of the western South American rift zone. However, carbonatite and kimberlite magmatism is exclusively known from the Ayopaya area.

The least evolved silicate variants from partial melting of metasomatised and carbonate-rich mantle are represented by melilititic and nephelinitic rocks. These are alkali- and carbonate-rich, predominantly sodic, and show high contents in some trace elements (e.g. REE). Such parental melts further evolve into the broad spectrum of alkaline igneous rocks that characterises the Ayopaya province. The Cerro Sapo complex portrays the complexity of carbonatite magmatism, with calciocarbonatite developing from carbonated nepheline syenite melt by liquid immiscibility. The latest stage of nepheline syenite formation on extended crystal fractionation leads to a highly evolved fluid- and carbonate-rich residual melt which produces the sodalite-ankerite-baryte dyke system. The bewildering variety of rocks of different petrogenetic processes in the Ayopaya alkaline province reinforces the comment by Bell et al. (1998) "...there are carbonatites and carbonatites".

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