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Oxygen and Carbon isotopes in the Barra do Itapirapuá and Mato Preto carbonatites (southern Brazil)

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RIASSUNTO – In generale le carbonatiti presentano ampi intervalli di variazioni riguardanti le composizioni isotopiche del carbonio e dell'ossigeno. Tali variazioni sono riconducibili sostanzialmente a (1) processi magmatici, (2) fenomeni idrotermali, (3) processi di contaminazione crostale (4) processi deuterici. Stabilire se l'entità delle variazioni isotopiche di carbonio e ossigeno è dovuta a processi primari o è relazionata a processi di contaminazione crostale può portare a importanti implicazioni relative alla valutazione del tipo di sorgente.

Il presente lavoro vuole fornire un modello di frazionamento isotopico O-C prendendo in considerazione due complessi carbonatitici del Bacino del Paraná (Brasile Meridionale), sulla base di tre considerazioni: (1) i complessi carbonatitici del Bacino del Paraná sono tra i più conosciuti nella letteratura internazionale dal punto di vista geologico e geochimico; (2) esiste una ricca casistica per quanto riguarda gli isotopi stabili (oltre 500 dati O-C) e una casistica significativa per quanto riguarda gli isotopi radiogenici; (3) è controversa l'interpretazione per quanto riguarda i processi di scambio isotopico, i.e. se «primari» o attribuibili a processi di contaminazione crostale.

A questo proposito sono state analizzate le composizioni isotopiche O-C di campioni di superficie e di carotaggi delle carbonatiti dei complessi di Barra do Itapirapuá e di Mato Preto. Le variazioni isotopiche, espresse in termini di $\delta^{18}\text{O}$ e $\delta^{13}\text{C}$, possono essere interpretate mediante scambio isotopico durante il processo di cristallizzazione frazionata del liquido carbonatitico e successivamente da scambi isotopici, in condizioni idrotermali, tra le rocce carbonatitiche e fluidi ricchi in $\text{H}_2\text{O}-\text{CO}_2$ a differenti temperature e con differenti rapporti $\text{H}_2\text{O}/\text{CO}_2$.

Termini chiave: Frazionamento isotopico, O-C, carbonatiti, Barra do Itapirapuá, Mato Preto, Brasile meridionale.

ABSTRACT – Carbonatitic complexes show large compositional ranges relative to the oxygen and carbon isotopes. The variations are attributable to (1) magmatic processes, (2) hydrothermal processes, (3) crustal contamination, (4) deuteric processes. Determining to what extent the oxygen and carbon isotopic variations in carbonatites are primary or related to crustal processes has important implications for evaluating the isotopic characteristics of the source regions.

In order to address some of these questions, a model of isotopic O-C fractionation relative to two Brazilian carbonatites from the Paraná Basin (Southern Brazil), is developed in this work. A favourable starting point of the model is the fact that the carbonatitic complexes from Paraná Basin are the best known in the worldwide literature from geological, petrological and geochemical points of view and that over 500 O-C isotopic data and a large number of radiogenic isotope compositions are nowadays available.

For this purpose, the oxygen and carbon isotopic compositions of carbonatites

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complexes from Barra do Itapirapuá and Mato Preto were analyzed on borehole and surface specimens. Variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ may be explained by isotopic exchange during fractional crystallization of the carbonatitic magma and by isotopic exchange between carbonatitic rocks and $\text{H}_2\text{O-CO}_2$ -fluids at different temperatures and with different $\text{H}_2\text{O/CO}_2$ ratios in hydrothermal conditions. The model of isotopic fractionation shows that the samples from Barra do Itapirapuá derive from magmatic crystallization ($\delta^{18}\text{O}$ from 8.0 to 10.0‰ and $\delta^{13}\text{C}$ from -7.5 to -5.0‰). The large isotopic variation of the specimens from Mato Preto ($\delta^{18}\text{O}$ from 8.3 to 18.9‰ and $\delta^{13}\text{C}$ from -6.3 to 0.8‰) may be produced in a magmatic environment and subsequently may be affected by hydrothermal processes starting from isotopic compositions $\delta^{18}\text{O} \sim 10$ and $\delta^{13}\text{C} \sim -5.0$ ‰.

Key words: O-C isotopic fractionation, carbonatites, Barra do Itapirapuá, Mato Preto, southern Brazil.

Introduction

Carbonatite complexes show large variations in the oxygen and carbon isotopes (e.g. Taylor et al., 1967; Pineau et al., 1973; Deines & Gold, 1973; Nelson et al., 1988; Censi et al., 1989; Deines, 1989; Santos & Clayton, 1995). The $\delta^{18}\text{O}$ values cover a wide range from about 5 to 25‰ vs SMOW (Deines, 1989), but 50% of the analyses fall in a narrow interval between 6 and 9‰. The variations in $\delta^{13}\text{C}$ are more restricted than those of $\delta^{18}\text{O}$ values: 91% of $\delta^{13}\text{C}$ values fall in the range between -2 and -8‰ vs PDB (Deines, 1989). Ranges of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ between 6 and 10‰ and between -4 and -8‰, respectively, are proposed for the «primary carbonatites» (cf. Taylor, 1967; Keller & Hoefs, 1995). Different emplacement levels (i.e. deep-seated, up to near surface, or surface environments; Deines & Gold, 1973) and superimposed «primary» and «secondary» processes are held to play a role in the isotopic variations. They may be attributed to (1) isotopic compositional differences in the source, (2) fractionation processes during magmatic evolution, (3) loss of fluids

during pressure reduction at the time of emplacement, (4) crustal contamination, (5) post-magmatic processes. The latter are due mainly to exchange with hydrothermal fluids and to influx of ground-water and isotopic exchange at low temperatures (Taylor et al., 1967; Pineau et al., 1973; Deines, 1989).

Determining to what extent the oxygen and carbon isotopic compositions in carbonatites are primary or secondary has important implications for evaluating the geochemical characteristics of the source regions. For example, the carbonatite complexes may be useful for deciphering the nature of the sub-continental mantle (e.g. Castorina et al., 1994 and 1997) because their high Nd and Sr abundances buffer the primary isotopic signatures against changes brought about by crustal contamination (Bell & Blenkinsop, 1989).

In order to address some of these questions, a model of isotopic O-C fractionation relative to two Brazilian carbonatites from the Paraná Basin (southern Brazil), i.e. Barra do Itapirapuá and Mato Preto carbonatites, is developed in this work. A favourable starting point of the model is the fact that the carbonatitic complexes from the Paraná Basin are

the best known in the worldwide literature from geological, petrological and geochemical point of view and over 500 O-C isotopic data and a lot of radiogenic isotope compositions are nowadays available (e.g. Nelson et al., 1988; Morikio et al., 1990; Castorina et al., 1994; 1997; Toyoda et al., 1994; Bizzi et al., 1994; Huang et al., 1995; Walter et al., 1995; Santos and Clayton, 1995; Ruberti et al., 1997a).

Regional framework

Geology, petrology and geochemistry of alkaline and alkaline-carbonatite com-

plexes in and around the Paraná Basin (southern Brazil) were recently reviewed by Morbidelli et al. (1995). Alkaline complexes from southern Brazil are distributed along tectonic lineaments (Fig. 1). Carbonatites are associated to K-alkaline complexes of Early- to Late Cretaceous age in the form of central elliptical intrusions or dykes (Rodrigues & Lima, 1984; Morbidelli et al., 1995; Comin-Chiaramonti & Gomes, 1996; Castorina et al., 1996). Previous studies yielded O-C isotopic results typical of «primary carbonatites» (Fig. 2), along with a number of higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures (Scheibe & Formoso, 1982; Nelson et al., 1988;

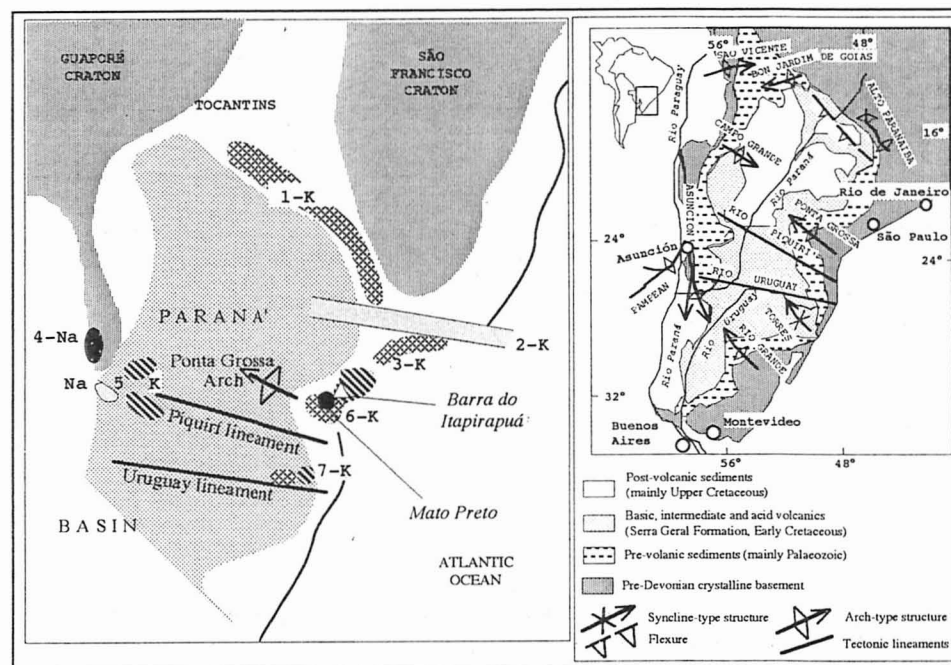


Fig. 1 - Main areas of alkaline complexes in and around the Paraná Basin. K, potassic complex; Na, sodic complex. 1, Alto Paranaíba (=85 Ma); 2, Taiuvá-Cabo Frio Lineament (<75 Ma); 3, Ribeira belt (70-116 Ma); 4, Alto Paraguay (245 Ma); 5, Paraguay (K:128 Ma, Na:<70 Ma); 6, Ponta Grossa Arch (118-138 Ma, north; 70-116 Ma, south); 7, Lages (70-75 Ma, west) and Anitópolis (129 Ma, east). I and II, Rio Piquiri lineament and Rio Uruguay lineament, respectively (Comin-Chiaramonti & Gomes, 1996). Inset: main geological features of the Paraná Basin (Comin-Chiaramonti et al., 1997).

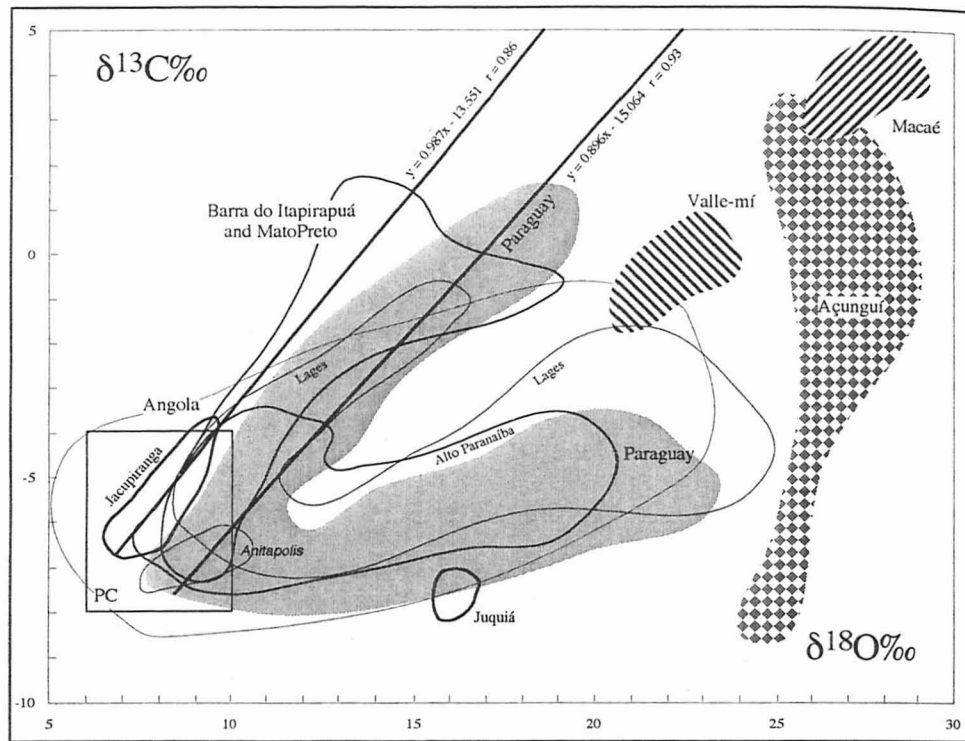


Fig. 2 - Distribution of $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ fields of carbonatites from the Paraná Basin, Southern Brazil (PC, «primary carbonatite box» from Taylor et al., 1967 and Keller & Hoefs, 1995). The regression lines are relative to «intrusive» environment (Castorina et al., 1997) Fields from carbonatic sediments are also shown (Açungui, precambrian metalimestones, Paraná State, Brazil: Santos & Clayton, 1995 and Censi, unpublished data; Valle-mi, Cambrian limestones-dolostones from eastern Paraguay: Castorina et al., 1994; Macaé, Albian-cenomanian limestones from Campos Basin, Rio de Janeiro State, Brazil: Robaina et al., 1991).

Censi et al., 1989; Morikiyo et al, 1990; Toyoda et al., 1994; Santos & Clayton, 1995; Walter et al., 1995; Castorina et al., 1994; 1996; 1997; Ruberti et al., 1997a, b,c). These enrichments in heavy isotopes were related to heterogeneity of the mantle source (Nelson et al., 1988), or to contamination by host rock (Santos & Clayton, 1995), or to magmatic vs hydrothermal evolution of the carbonatite at shallow level (Censi et al., 1989). Three successive stages of crystallization (magmatic, late magmatic and hydrothermal)

were distinguished by Walter et al. (1995) in the Juquiá carbonatite (Ponta Grossa Arch, 127 Ma), where the first stage corresponds to the crystallization of magmatic Fe-dolomite. Notably, the samples from boreholes or quarries show $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ positive correlations (Fig. 2), Juquiá carbonatite excepted, with slopes between 0.9 (e.g. Paraguay well; Castorina et al., 1997) and 1.0 (e.g. Jacupiranga; Huang et al, 1995) and a correlation coefficient close to 0.9. Specimens from outcrops are generally poorly correlated

and show heavy oxygen increments of more than $\delta^{18}\text{O}$ (slope < 0.4).

Initial Nd and Sr isotope ratios relative to the carbonatites from Paraná Basin lato sensu (i.e. including occurrences from Paraguay and Angola) indicate isotopic signatures similar to those of the associated alkaline and tholeiitic rock-types. They are between HIMU (high- $^{238}\text{U}/^{204}\text{Pb}$ mantle end-member) and EM I (enriched mantle-I end-member; Zindler & Hart, 1986) mantle components (Fig.

3). These features were interpreted as due to lithospheric mantle sources which suffered different metasomatic events in time and space, without appreciable effects of crustal contamination (Castorina et al., 1994; 1997; Comin-Chiaramonti et al., 1995 and 1998). It must be noted that Sr-Nd isotopic values of Barra do Itaipapuá and Mato Preto carbonatites overlaps the same fields of Early Cretaceous tholeiites and alkaline rocks from Ponta Grossa Arch and Angola-Namibia (Fig. 3).

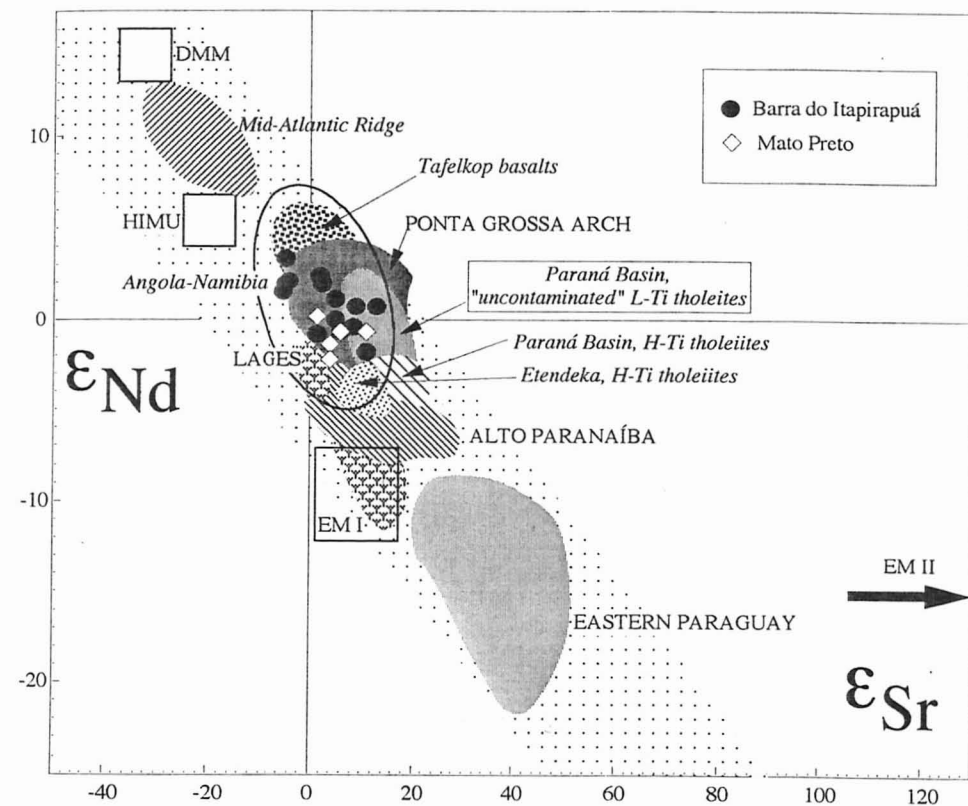


Fig. 3 - Sr-Nd isotopic ratios («time integrated» ϵ -notation) of selected carbonatite specimens from Barra do Itaipapuá and Mato Preto compared with Sr-Nd isotopes relative to the Mesozoic magmatic rocks from the Paraná Basin (Comin-Chiaramonti et al., 1997 and references therein) DMM, depleted mantle; HIMU, high $^{238}\text{U}/^{204}\text{Pb}$ mantle end-member; EM I and EM II enriched mantle I and II component, respectively (e.g. Zindler & Hart, 1986).

Oxygen and carbon isotope abundances of the carbonatites from Barra do Itapirapuá - BI- (Mg-Fe carbonatite, notional age: 129 Ma) and from Mato Preto - MP- (Ca-carbonatite, notional age: 70 Ma), on the eastern side of the Ponta Grossa Arch (Fig. 1), were investigated with the aim of modelling the isotopic signature in terms of magmatic origin followed by hydrothermal evolution. The BI and MP carbonatites occur as plugs or veins and comprise only a minor part of larger plutonic to subvolcanic K-alkaline complexes that intrude Precambrian rocks (i.e. «Tres Corregos granites» and metasediments of the «Açungui Group»; Almeida, 1983; Ruberti et al., 1997b, c) in the easternmost side of the «Ponta Grossa Arch». This arch is also characterized by widespread tholeiitic magmatism of Early Cretaceous age (Piccirillo et al., 1990).

Notably, Santos & Clayton (1995) suggested that the large isotopic variations, such as those in MP and BI carbonatites, may have been produced by contamination from the country metalimestones (e.g. Mato Preto carbonatite) and/or by post-crystallization alteration (e.g. Barra do Itapirapuá carbonatite).

Samples and methods

The samples make up a representative selection of carbonatites from six boreholes (43 specimens) of Barra do Itapirapuá and one borehole (6 specimens) and outcrop samples (9 specimens) from Mato Preto; 14 additional specimens from Mato Preto are quoted in Santos & Clayton (1995). The whole-rock compositions were determined by standard

chemical and XRF methods (e.g. Castorina et al., 1996), and recalculated as calcite-dolomite-ankerite wt% (Table 1). The oxygen and carbon isotopic compositions on carbonates were obtained by reacting the samples with 100% H₃PO₄ at 25°C. The released CO₂ was subsequently analyzed in a Finnigan Mat Delta S mass spectrometer and its oxygen isotopic composition has been corrected to calcite and dolomite by applying the fractionation factors 1.01025 and 1.0111, respectively according to Santos & Clayton (1995). Since most of the samples contain both calcite and Fe-dolomite (ankeritic dolomite), they were analyzed using the double extraction technique described by Epstein & Taylor (1967). The sample powders were prepared with grain size fractions ranging between 100 and 200 mesh. The CO₂ corresponding to calcite and dolomite was extracted after 1 hour and between 24 and 384 hours after reaction, respectively. The isotopic results are given in terms of usual ‰ units, the reference standards being PDB-1 for carbon and V-SMOW for oxygen (Table 1).

Oxygen and Carbon isotopes

The isotopic results are diagrammatically shown in Figures 4A and B in terms of δ¹⁸O vs δ¹³C.

In the carbonatite from the Barra do Itapirapuá complex, Fe-dolomite is an ubiquitous phase: all samples are characterized by Fe-dolomite, 95% of the population having more than 60 wt%, and 44% of the specimens show coexisting calcite and Fe-dolomite (cf Table 1). In Fe-dolomite, δ¹⁸O ranges between 8.54 and 17.53‰ (av. 10.12 ± 2.00) and

TABLE 1
Carbon and oxygen isotopic values for carbonatites from Barra do Itapirapuá and Mato Preto; (***), data from Santos & Clayton (1995). The standard deviation of the whole analytical procedure is about ±0.05‰ (1σ) for both carbon and oxygen. The wt% composition is also reported as calcite = calc, dolomite = dol and ankerite = ank is also reported.

BARRA DO ITAPIRAPUÁ	δ ¹⁸ O dol/ank	δ ¹³ C dol/ank	δ ¹⁸ O calc	δ ¹³ C calc	calc% wt	dol% wt	ank% wt	BARRA DO ITAPIRAPUÁ			MATO PRETO						
								δ ¹⁸ O dol/ank	δ ¹³ C dol/ank	δ ¹⁸ O calc	δ ¹³ C calc	calc% wt	dol% wt	ank% wt			
Drill 01																	
6196(-32.5m)	8.64	-6.19	7.91	-6.65	14.0	50.1	35.9	9.36	-5.85	8.65	-6.35	19.2	41.4	39.4			
6197(-39.3m)	9.00	-5.78	7.4	5.85	34.1	66.7	27.2	5214(-6.8m)	9.13	-5.76	-6.35	4.6	80.8	14.6			
6174(-66.5m)	8.87	-6.13	7.24	7.95	18.1	74	34.1	8.76	-6.22			0.1	82.3	17.6			
6198(-87.4m)	9.37	-5.69	1.7	6.87	29.6	61.90(-66m)	10.19	9.23	-5.71			3.2	73.7	23.1			
6199(-100.7m)	8.85	-6.20	0.1	8.37	16.2	6191(-78.8m)	8.63	10.19	-3.69			0.8	79.1	20.1			
6200(-128.7m)	9.28	-6.31		8.34	16.6	6192(-95m)	8.73	8.73	-6.52				76.2	23.8			
6201(-188.6m)	8.97	-6.58		7.64	20.5	6193(-99.7m)	9.81	9.81	-6.04				74.9	25.1			
Drill 02								14.74	1.18			4.1	73.9	20.0			
6203(-43.28m)	9.17	-6.04		8.04	18.7	6195(-141m)	9.72	9.72	-5.40			2.0	68.3	29.7			
6175(-72.4m)	8.84	-6.13	9.71	-5.05	27.5	36.5	36.0										
6202(-76.65m)	10.69	-4.99		5.05	27.5	36.5	36.0										
6204(-95.5m)	9.69	-5.19		4.43	3.4	73.4	26.9										
6176(-110.5m)	9.97	-4.43	8.80	-6.12	20.5	52.6	26.9										
6177(-115.5m)	9.24	-5.75						11.88	-2.74								
Drill 03																	
6178(-35.7m)	15.55	-0.3	12.64	-0.89	84.6	12.2	3.2										
6180(-72.7m)	17.25	-0.2	16.08	-1.30	63.8	80.2	19.8										
6205(-72.2m)	8.54	-6.98															
6206(-93.6m)	12.63	-1.95	8.85	-6.04	15.6	58.2	26.2										
6207(-142m)	9.9	-5.72	8.70	-6.28	7.5	64.9	27.6										
6208(-183.4m)	9.26	-6.00															
Drill 05																	
6180(-40m)	9.41	-5.65	8.43	-6.00	12.0	66.6	21.4										
6209(-61.2m)	10.18	-5.57	9.05	-6.03	24.7	57.7	17.6										
6181(-79m)	10.00	-5.19	9.06	-5.82	15.3	62.7	22.0										
6182(-87.3m)	13.26	1.42	12.55	0.81	7.6	78.0	14.4										
6183(-90.4m)	14.13	1.38			3.5	83.9	12.6										
6184(-98m)	9.08	-6.35			4.8	63.1	32.1										
6210(-130m)	10.12	-5.34	9.13	-5.50	39.0	34.0	27.0										
6211(-150m)	9.30	-6.67	8.51	-7.04	7.9	67.6	24.5										
6185(-160.5m)	9.36	-5.99	8.80	-6.36	7.1	51.4	41.5										
6186(-172.3m)	9.09	-6.03	8.60	-6.61	13.0	55.0	32.0										
6187(-190m)	9.14	-5.38	8.95	-5.90	18.5	43.6	37.9										
6212(-210m)	9.64	-4.99	9.88	-5.38	25.3	53.9	20.8										
6213(-230m)	10.55	-5.94															
6370(-256m)	9.60		9.09	-6.43	7.9	68.4	23.7										
Surface samples																	
6269(-50.7m)																	
7-DB46-A																	
8-DB46-B																	
DB45-8733A-B																	
DB47-8747-B																	
DB47-8748																	
DB47-8751-B																	
DB47-8754-B																	
SR-301-A																	
SR-501-8778-B																	
SR-502-8780-B																	
SR-501-8781-B																	
SR-501-8773-C																	

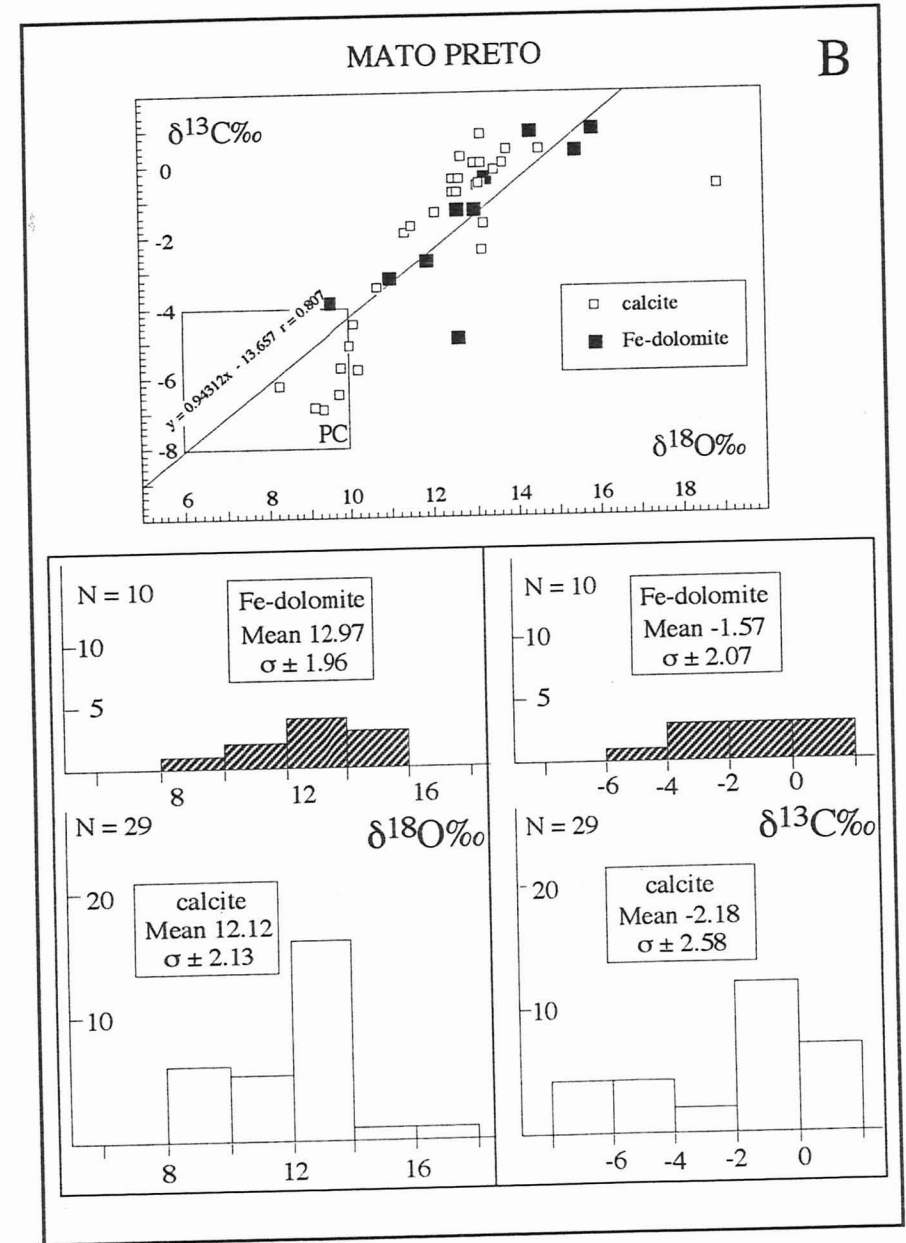
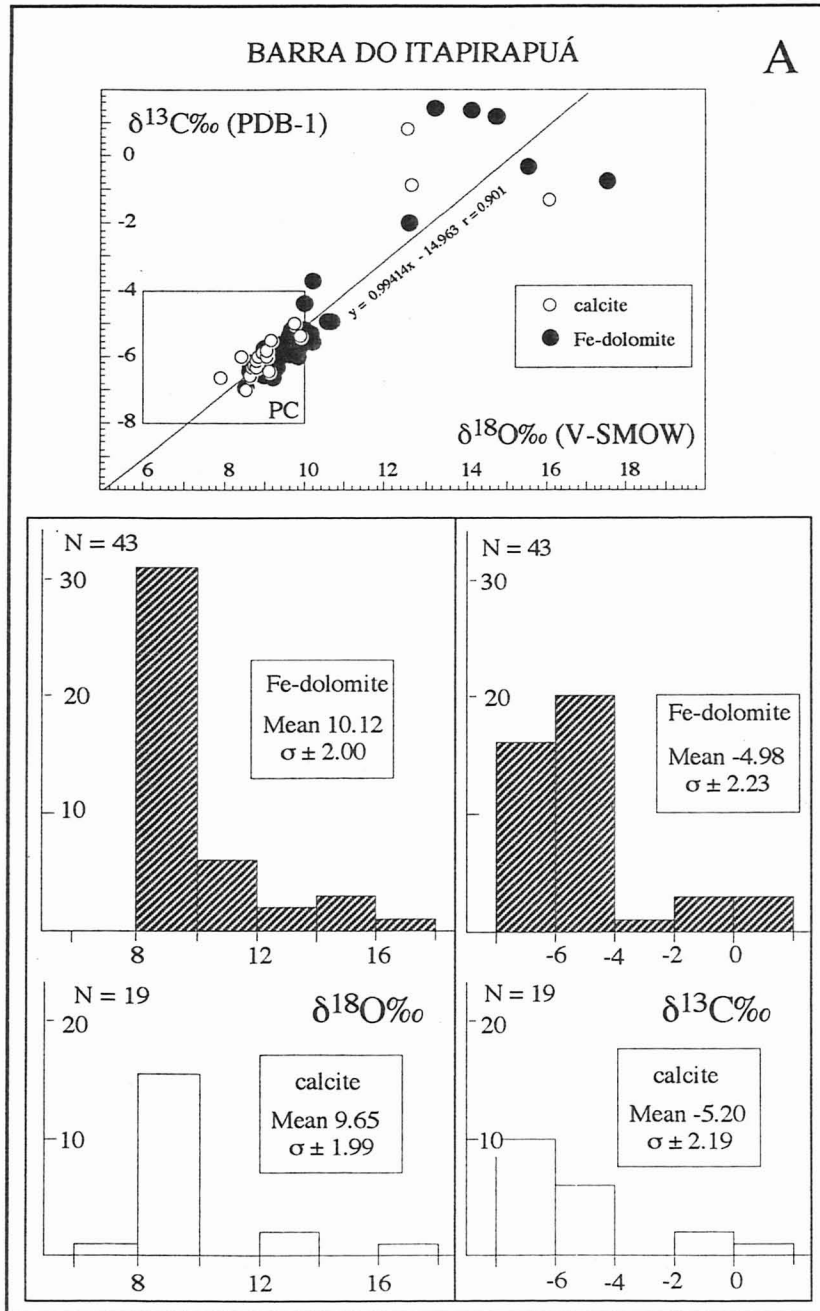


Fig. 4 - Plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the carbonatites from Barra do Itaipirapuá (A) and Mato Preto (B), Southern Brazil (PC, «primary carbonatite box» from Taylor et al., 1967 and Keller & Hoefs, 1995), and relative distribution histograms.

$\delta^{13}\text{C}$ between -6.98 and 1.42‰ (av. -4.98 ± 2.23); in calcite, $\delta^{18}\text{O}$ ranges between 7.91 and 16.08‰ (av. 9.65 ± 1.99), and $\delta^{13}\text{C}$ between -7.04 and 0.81 (av. -5.20 ± 2.19). The isotopic data fit a straight line (slope = 0.99 , $r = 0.90$), and 79% of the carbonates plot within or close to the «primary» magmatic carbonatite box (Fig. 4A).

In the carbonatite from the *Mato Preto* complex, 98% of the sample population shows calcite, 28% displaying associated calcite and Fe-dolomite. Fe-dolomite is the main phase in 10% of samples. In Fe-dolomite, $\delta^{18}\text{O}$ ranges between 9.50 and 15.91‰ (av. 12.97 ± 1.96) and $\delta^{13}\text{C}$ ranges between -4.98 and 0.95‰ (av. -1.57 ± 2.07). In calcite, $\delta^{18}\text{O}$ ranges between 8.26 and 18.09‰ (av. 12.12 ± 2.13), and $\delta^{13}\text{C}$ ranges between -6.94 and 0.80‰ (av. -2.18 ± 2.58). The isotopic data fit a straight line (slope = 0.94 , $r = 0.81$) similar to the correlation shown by the Barra do Itaipirapuá carbonatite samples, but in this case only 23% of the carbonates plot within or close to the «primary» magmatic carbonatite box (Fig. 4B).

Correlations between isotopic compositions and depth are not apparent both in the Barra do Itaipirapuá and in the Mato Preto carbonatites (Fig. 5). The isotopic data appear to be an extension of the Jacupiranga carbonatite, which is believed to have a primary signature (Huang et al., 1995). They fit the distribution pattern of values in primary carbonates from the boreholes drilled in eastern Paraguay (Castorina et al., 1997; Fig. 2).

Notably, Fe-dolomite has higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than coexisting calcite, both in the Barra do Itaipirapuá and in

the Mato Preto carbonatites (Fig. 5). The carbonates from Barra do Itaipirapuá display a bimodal distribution, whereas the Mato Preto samples share a continuous variation for both Fe-dolomite and coexisting calcite (Figs. 5 and 6). The averaged $\Delta^{18}\text{O}_{\text{Fe-dolomite-calcite}}$ and $\Delta^{13}\text{C}_{\text{Fe-dolomite-calcite}}$ are 1.08 ± 0.57 and 0.43 ± 0.21 , respectively (Barra do Itaipirapuá: $\Delta^{18}\text{O}_{\text{Fe-dolomite-calcite}} = 0.94 \pm 0.55$, $\Delta^{13}\text{C}_{\text{Fe-dolomite-calcite}} = 0.43 \pm 0.16$; Mato Preto: $\Delta^{18}\text{O}_{\text{dolomite-calcite}} = 1.43 \pm 0.49$, $\Delta^{13}\text{C}_{\text{dolomite-calcite}} = 0.44 \pm 0.38$). On the basis of available O-C isotopic data from carbonate minerals, equilibrium isotopic fractionation between calcite and dolomite should produce only a small enrichment in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of dolomite at relatively high temperatures (e.g. $\sim 500^\circ\text{C}$).

The difference in isotopic composition between coexisting Fe-dolomite and calcite, as well as the relationship which would be expected if coexisting carbonates were formed in isotopic equilibrium (Sheppard & Schwarz, 1970: metamorphic equilibrium; Deines, 1989: fractionation processes at about 700°C), is shown in Fig. 6. The data are not consistent with the existence of isotopic equilibrium at magmatic temperatures between coexisting Fe-dolomite and calcite, although a roughly equilibrium between the variables is apparent. This fact might indicate metasomatic changes at low temperatures, not far from hydrothermal conditions (i.e. $\leq 375^\circ\text{C}$ and $P = 1$ atm). Sub-solidus groundwater interaction might be an explanation for the $\delta^{18}\text{O}$ values of carbonates higher than 12‰ from Mato Preto and Barra do Itaipirapuá. The known carbonate- H_2O oxygen fractionation values (e.g. Deines, 1989, and therein

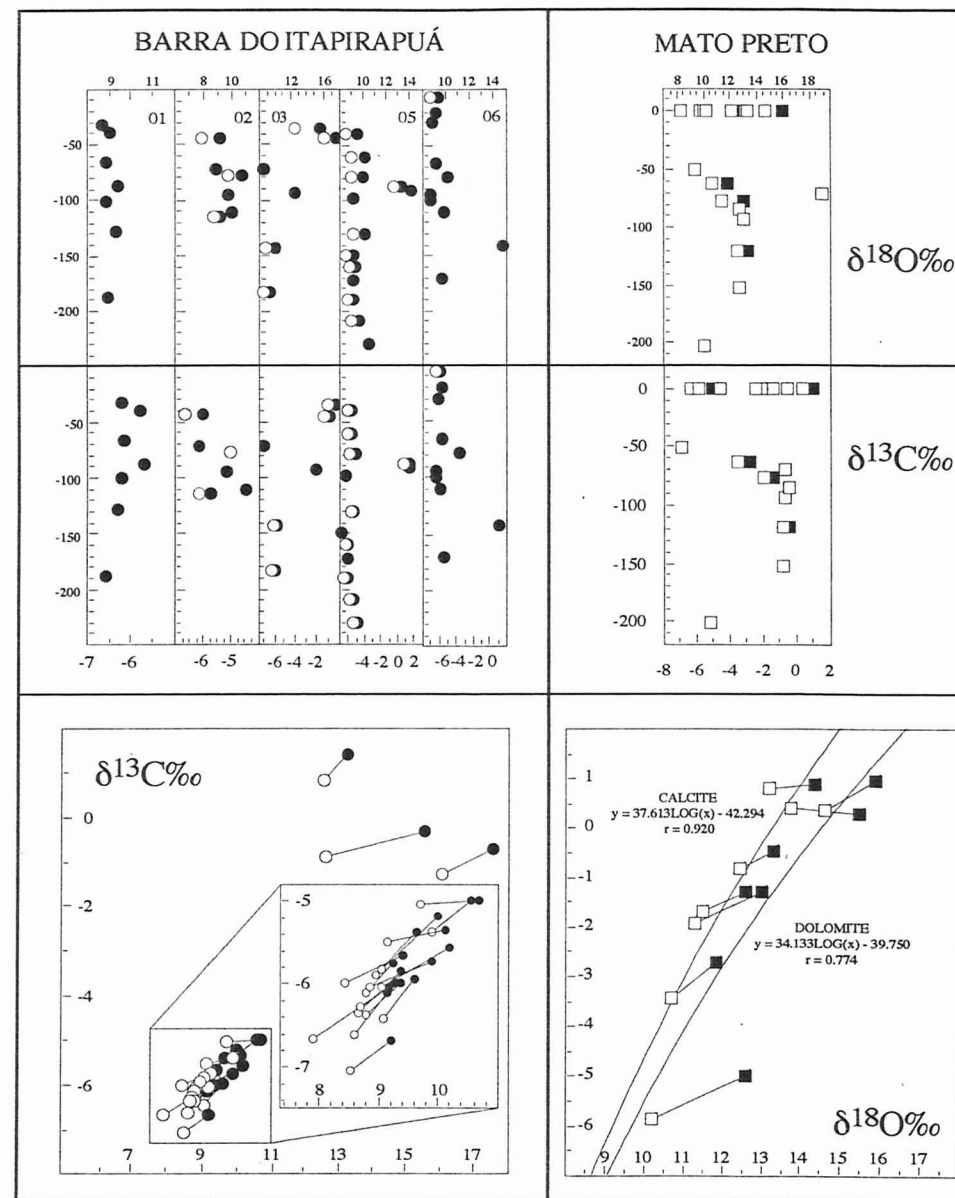


Fig. 5 - Distribution of O-C isotopic data of the carbonatites from Barra do Itaipirapuá and Mato Preto vs. depth. The values relative to coexisting calcite (open symbols) and Fe-dolomite (full symbols) are also shown.

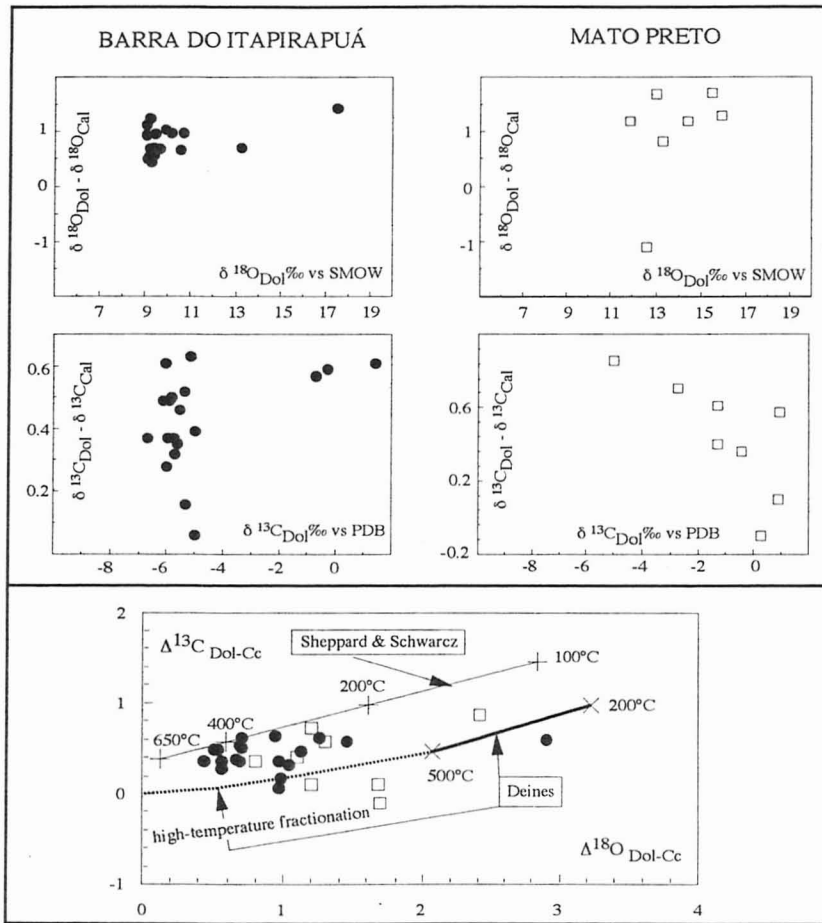


Fig. 6 - Plot of $\delta^{18}\text{O}_{\text{Dolomite}}$ and $\delta^{13}\text{C}_{\text{Dolomite}}$ vs $\delta^{13}\text{C}_{\text{Calcite}}$ ($\Delta^{13}\text{C}_{\text{dol-cal}}$) $\delta^{18}\text{O}_{\text{Dolomite}} - \delta^{18}\text{O}_{\text{Calcite}}$ ($\Delta^{18}\text{O}_{\text{dol-cal}}$) and $\delta^{13}\text{C}_{\text{Dolomite}}$ and $\delta^{13}\text{C}_{\text{Calcite}}$ ($\Delta^{13}\text{C}_{\text{dol-cal}}$), respectively, for coexisting calcite-dolomite pairs. Equilibrium lines, metamorphic and magmatic-hydrothermal, are from Sheppard & Schwarz (1970), and from Deines (1989), respectively. Full symbols and open symbols represent samples from Barra do Itaipirapuá and Mato Preto, respectively.

references) and the typically negative $\delta^{18}\text{O}$ -values for meteoric groundwaters (e.g. Hoefs, 1987) require that any interaction with groundwater must have occurred at low temperatures (<250°C; Deines, 1989). Alteration of Fe-dolomite by groundwater may be related to the low-temperature hydrothermal cycle (112-

150°C; Roedder, 1973) responsible for the formation of the massive fluorite deposits, as the Mato Preto (and Barra do Itaipirapuá) carbonatite emplacement and the fluorite deposition are closely related in time (Santos et al, 1996; Ruberti et al., 1997b, c).

On the whole, the data support the hy-

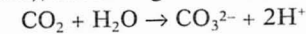
pothesis that isotopic re-equilibrations may have occurred both during a magmatic stage and the subsequent hydrothermal stage. A model regarding the whole evolution of the isotopic O-C compositions from the two carbonatites is developed in the next section.

Model of isotopic fractionation

1. Magmatic evolution

Hypothesis:

A) crystallization of the carbonatitic liquid under nearly closed conditions, in the temperature interval from 700°C and to about 400°C (e.g. Kuellmer et al., 1966; Wyllie, 1989 and therein references), according to the reaction:



The initial isotopic composition are assumed to have been $\delta^{18}\text{O} = 8.0$ and $\delta^{13}\text{C} = -7.5\text{‰}$;

B) only CO_2 and H_2O are oxygen carriers, and CO_2 is carbon carrier too;

C) mass balance equations for oxygen and carbon are:

$$[1] \quad 2\mathbf{A}\delta^{18}\text{O}_{(\text{CO}_2)^i} + \mathbf{B}\delta^{18}\text{O}_{(\text{H}_2\text{O})^i} = 2\mathbf{a}\delta^{18}\text{O}_{(\text{CO}_2)} + 3\mathbf{b}\delta^{18}\text{O}_{(\text{cc})} + \mathbf{c}\delta^{18}\text{O}_{(\text{H}_2\text{O})} \text{ and}$$

$$[2] \quad \mathbf{A}\delta^{13}\text{C}_{(\text{CO}_2)^i} = \mathbf{a}\delta^{13}\text{C}_{(\text{CO}_2)} + \mathbf{b}\delta^{13}\text{C}_{(\text{cc})}$$

where \mathbf{a} , \mathbf{b} , \mathbf{c} are CO_2 , CO_3^{2-} and H_2O molar concentrations in the fluid-mineral system at time «t». \mathbf{A} and \mathbf{B} are the initial CO_2 and H_2O molar concentrations, respectively, in the magmatic fluid at «i» before crystallization of the carbonate (cc) (i.e., fixed \mathbf{A} , from $\text{CO}_2/\text{H}_2\text{O}$ initial molar ratio, \mathbf{B} is defined). From the above equations the concentration values

of the various components can be defined at each time «t» as $\mathbf{b} = \mathbf{A} - \mathbf{a}$ and $\mathbf{c} = \mathbf{B} - \mathbf{b}$. It follows that the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compositions of the carbonate can be written in terms of \mathbf{a} , \mathbf{b} and \mathbf{c} , as well as of fractionation factors $\Delta^{18}\text{O}_{(\text{CO}_2-\text{cc})}$, $\Delta^{18}\text{O}_{(\text{cc}-\text{H}_2\text{O})}$ and $\Delta^{13}\text{C}_{(\text{CO}_2-\text{cc})}$ (Bottinga, 1968; O'Neil et al., 1969), according to the equations:

$$[3] \quad \delta^{18}\text{O}_{(\text{cc})} = [2\mathbf{A}\delta^{18}\text{O}_{(\text{CO}_2)^i} + \mathbf{B}\delta^{18}\text{O}_{(\text{H}_2\text{O})^i} - 2\mathbf{a}\Delta^{18}\text{O}_{(\text{CO}_2-\text{cc})} + \mathbf{c}\Delta^{18}\text{O}_{(\text{cc}-\text{H}_2\text{O})}] / [3\mathbf{b} + 2\mathbf{a} + \mathbf{c}]$$

$$[4] \quad \delta^{13}\text{C}_{(\text{cc})} = [\mathbf{A}\delta^{13}\text{C}_{(\text{CO}_2)^i} - (\mathbf{A} - \mathbf{b})\Delta^{13}\text{C}_{(\text{CO}_2-\text{cc})}] / \mathbf{A}.$$

Numerical calculations are reported in Table I of the Appendix.

2. Fluid-related hydrothermal recrystallization

After the crystallization of primary carbonates, recrystallization occurs by interactions with hydrothermal fluids at $T < 400^\circ\text{C}$. According to Zheng & Hoefs (1993), isotopic effects may be described by the equation:

$$[5] \quad \delta^{18}\text{O}_{(\text{cc})} = (\delta^{18}\text{O}_{(\text{H}_2\text{O})^i} + \Delta^{18}\text{O}_{(\text{cc}-\text{H}_2\text{O})}) - [(\delta^{18}\text{O}_{(\text{H}_2\text{O})^i} + \Delta^{18}\text{O}_{(\text{cc}-\text{H}_2\text{O})}) - \delta^{18}\text{O}_{(\text{cc})^i}] \exp(-W/R_{(\text{O})})$$

$$[6] \quad \delta^{13}\text{C}_{(\text{cc})} = (\delta^{13}\text{C}_{(\text{HCO}_3)^i} + \Delta^{13}\text{C}_{(\text{cc}-\text{HCO}_3)}) - [(\delta^{13}\text{C}_{(\text{HCO}_3)^i} + \Delta^{13}\text{C}_{(\text{cc}-\text{HCO}_3)}) - \delta^{13}\text{C}_{(\text{cc})^i}] \exp(-W/R_{(\text{C})} \chi_{(\text{HCO}_3)})$$

with $\delta^{18}\text{O}_{(\text{cc})}$ and $\delta^{13}\text{C}_{(\text{cc})}$: initial isotopic composition of the carbonate; $\delta^{13}\text{C}_{(\text{HCO}_3)^i}$: initial carbon isotopic composition of HCO_3^- in the fluid; $\chi_{(\text{HCO}_3)}$: molar fraction HCO_3^- in the fluid; $W/R_{(\text{O})}$ and $W/R_{(\text{C})}$: water/rock ratios in atom percentages of oxygen and carbon in the fluid and rock, and related to the calcite solubility product (K_{ps}) that depends on temperature according to the equation (Jacobson &

Langmuir, 1974):

$$[7] \log K_{ps} = -13.870 - 3059 / T \text{ } ^\circ\text{K} - 0.04035 * T \text{ } ^\circ\text{K}$$

As well as the W/R ratios, also the HCO_3^- molar fraction in the fluid is a function of the temperature, due to the equilibria $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$ (K_0), $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ (K_1), $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ (K_2) and related equilibrium constants:

$$[8] \log K_0 = -14.0184 + 2385.73/T \text{ } ^\circ\text{K} + 0.0152642 * T \text{ } ^\circ\text{K} \text{ (Harned \& Davis, 1943)}$$

$$[9] \log K_1 = 14.8435 + 3404.71/T \text{ } ^\circ\text{K} - 0.032786 * T \text{ } ^\circ\text{K} \text{ (Harned \& Davis, 1943)}$$

$$[10] \log K_2 = 6.498 - 2902.39/T \text{ } ^\circ\text{K} - 0.02379 * T \text{ } ^\circ\text{K} \text{ (Harned \& Sholes, 1941)}$$

where the carbon speciation depends on the temperature and the pH. The initial $\delta^{13}\text{C}(\text{HCO}_3^-)_i$ can be calculated from the isotopic fractionation factors relative to $\Delta^{13}\text{C}(\text{CO}_2\text{-HCO}_3^-)$ (Ohmoto & Rye, 1979), for various $\delta^{13}\text{C}$ values calculated for CO_2

in the fluid. Numerical calculations are shown in Table II of the Appendix, and the model is graphically represented in Fig. 7, where a continuous variation of intensive parameters (i.e. $f = [(A-b)/A]$) can be noticed.

Concluding remarks

The application of the model to the observed oxygen and carbon isotopic data allows some considerations. The isotopic compositions of the carbonatite from Barra do Itaipirapuá appear to be in agreement essentially with a magmatic origin (box «I» of Fig. 7) from hypercritical fluids with $\text{CO}_2/\text{H}_2\text{O} \sim 0.6$ molar ratios and temperatures ranging from 700 to 400°C (i.e. «orthomagmatic vs pegmatitic» environment; e.g. Wyllie, 1989). Only a few samples would seem to have been altered by late hydrothermal process (paths of box «II» of Fig. 7). On the other hand, most carbonatite specimens

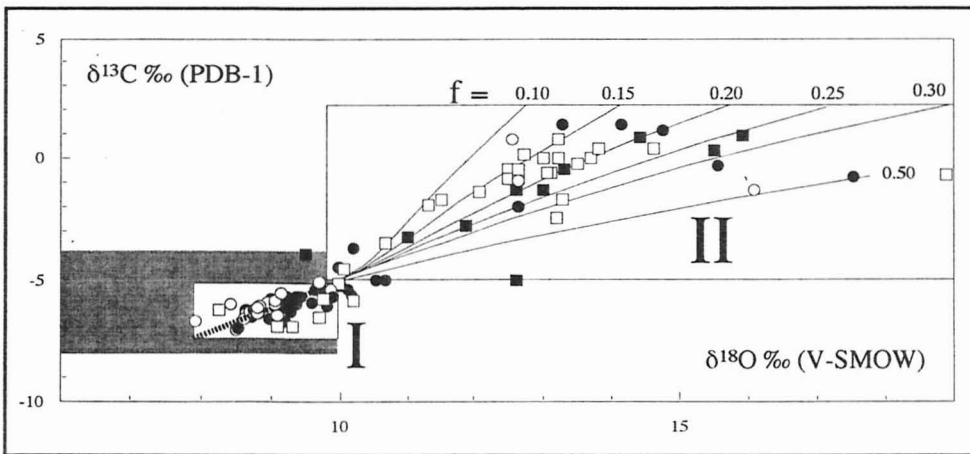


Fig. 7 - Comparison of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the studied specimens with the results from the elaborated model. $f = [(A-b)/A]$; see text and Table II.

from Mato Preto look as hydrothermally altered. Addition in the system of carbonates from the country rocks (e.g. «Açunguá Group»: $\delta^{18}\text{O} = +25.0 \text{ } \rightarrow \text{ } +24.4\text{ } \text{‰}$; $\delta^{13}\text{C} = +3.5 \text{ } - \text{ } -8.6\text{ } \text{‰}$) as suggested by Santos & Clayton (1995), appears to be unnecessary to explain samples considerably enriched in both heavy oxygen and carbon. This interpretation is also supported by the initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios in selected carbonatites that maintain the same values of the associated alkaline rocks (averaged $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ initial ratios, respectively, for both alkaline complexes and carbonatites: 0.7049 ± 0.0005 and 0.51253 ± 0.00007 , Barra do Itaipirapuá; 0.7048 ± 0.0003 and 0.51247 ± 0.00016 , Mato Preto; Ruberti et al., 1997a, b, c; Castorina & Comin-Chiaramonti, unpublished data), and are similar to the values obtained for the Early Cretaceous tholeiites of the Serra Geral Formation of the region (Comin-Chiaramonti et al., 1997). Moreover, the model ages referred

to the depleted mantle are 553 ± 119 and 559 ± 66 Ma for carbonatites from Barra do Itaipirapuá and Mato Preto, respectively (Ruberti et al., 1997a), in agreement with the mantle events characterizing the source of Early Cretaceous alkaline complexes at the latitude of Ponta Grossa Arch (e.g. Comin-Chiaramonti et al., 1997; Castorina et al., 1994; 1997). This means that the carbonatites maintained the mantle source characteristics in terms of radiogenic isotopes, even if their original O-C isotopic signatures were in part modified by post-depositional hydrothermal fluids at low temperature.

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Appendix

Oxygen-carbon modelling (cf Tables I and II) for magmatic and hydrothermal evolution of carbonatites was carried out using Microsoft Excel 5 program. The program is available on request as worksheet to P. Censi (Istituto di Mineralogia, Petrografia e Geochimica, Università di Palermo, via Archirafi, 36, I-90123, Palermo, Italy).

TABLE I

Oxygen and carbon model for magmatic evolution of the carbonatitic liquid. The model expects that during «high temperature» stage the carbonate crystallization takes place between 700 and 400 °C.

$\delta^{18}O_i$		$\delta^{13}C_i$ (CO_2/H_2O) _i									
a	c	b									
(CO_2) _f	(H_2O) _f	($CaCO_3$)	$\delta^{18}O(cc)_f$	$\delta^{13}C(cc)_f$	$\delta^{18}O(H_2O)_f$	$\delta^{18}O(CO_2)_f$	$\delta^{13}C(CO_2)_f$	T °C			
100.00	166.67	0.00	8.00	-7.50	7.55	13.72	-5.24	700			
95.00	161.67	5.00	8.05	-7.41	7.69	13.88	-5.12	685			
90.00	156.67	10.00	8.11	-7.32	7.84	14.05	-5.01	670			
85.00	151.67	15.00	8.17	-7.22	8.01	14.23	-4.89	655			
80.00	146.67	20.00	8.19	-7.12	8.19	14.42	-4.77	640			
75.00	141.67	25.00	8.31	-7.02	8.37	14.61	-4.65	625			
70.00	136.67	30.00	8.40	-6.91	8.57	14.82	-4.52	610			
65.00	131.67	35.00	8.48	-6.80	8.78	15.04	-4.40	595			
60.00	126.67	40.00	8.58	-6.69	9.01	15.26	-4.27	580			
55.00	121.67	45.00	8.68	-6.58	9.25	15.50	-4.14	565			
50.00	116.67	50.00	8.79	-6.46	9.51	15.74	-4.02	550			
45.00	111.67	55.00	8.91	-6.34	9.78	16.00	-3.89	535			
40.00	106.67	60.00	9.04	-6.22	10.07	16.27	-3.77	520			
35.00	101.67	65.00	9.17	-6.10	10.37	16.55	-3.64	505			
30.00	96.67	70.00	9.32	-5.97	10.70	16.85	-3.52	490			
25.00	91.67	75.00	9.47	-5.85	11.05	17.15	-3.40	475			
20.00	86.67	80.00	9.64	-5.73	11.42	17.48	-3.29	460			
15.00	81.67	85.00	9.81	-5.60	11.82	17.81	-3.18	445			
10.00	76.67	90.00	10.00	-5.48	12.24	18.17	-3.08	430			
5.00	71.67	95.00	10.20	-5.36	12.68	18.53	-2.99	415			
0.00	66.67	100.00	10.41	-5.24	13.16	18.92	-2.91	400			

TABLE II
Oxygen and carbon model for hydrothermal evolution of a carbonatitic rock. «f» is the residual fraction of fluid defined by $f = [(A-b) / A]$ (see text). The model expects that the residual fluid fraction, remained after the «high temperature» stage, is involved in the hydrothermal stage at temperature ≤ 375 °C. In this residual fluid fraction, the amount of dissolved CO_2 as $[CO_2]$, is related to the variation of CO_2 fraction in the late magmatic fluid, that is «f».

$\delta^{13}C_i$ (HCO_3)		$[CO_2]$													
K ₀	K ₁	K ₂	K _{ps}	[H_2CO_3]	pH	[HCO_3]	Solubility of calcite	W/R (C)	X(HCO_3)	W/R (O)	T °C	$\delta^{18}O_{cc}$	$\delta^{13}C_{cc}$		
3.58E-01	2.21E-12	4.01E-14	1.01E-17	7.20E-01	5.90	1.26E-06	2.51E-04	3.48E-04	1.75E-06	1.36E-05	375	9.76	-5.46		
3.07E-01	3.28E-12	5.26E-14	1.71E-17	6.18E-01	5.85	1.42E-06	3.26E-04	5.27E-04	2.30E-06	1.76E-05	368	9.76	-5.46		
2.64E-01	4.86E-12	6.87E-14	2.91E-17	5.31E-01	5.79	1.61E-06	4.23E-04	7.96E-04	3.03E-06	2.28E-05	361	9.76	-5.46		
2.28E-01	7.19E-12	8.97E-14	4.92E-17	4.57E-01	5.74	1.81E-06	5.48E-04	1.20E-03	3.96E-06	2.96E-05	354	9.76	-5.46		
1.96E-01	1.06E-11	1.17E-13	8.30E-17	3.95E-01	5.69	2.04E-06	7.12E-04	1.80E-03	5.18E-06	3.85E-05	347	9.76	-5.46		
1.70E-01	1.55E-11	1.51E-13	1.40E-16	3.42E-01	5.64	2.30E-06	9.23E-04	2.70E-03	6.75E-06	4.99E-05	340	9.76	-5.46		
1.47E-01	2.27E-11	1.96E-13	2.34E-16	2.96E-01	5.59	2.60E-06	1.20E-03	4.04E-03	8.76E-06	6.47E-05	333	9.76	-5.46		
1.28E-01	3.32E-11	2.53E-13	3.92E-16	2.57E-01	5.53	2.92E-06	1.55E-03	6.03E-03	1.14E-05	8.39E-05	326	9.76	-5.46		
1.12E-01	4.82E-11	3.25E-13	6.54E-16	2.24E-01	5.48	3.29E-06	2.01E-03	8.97E-03	1.47E-05	1.09E-04	319	9.76	-5.46		
9.76E-02	6.98E-11	4.16E-13	1.09E-15	1.96E-01	5.43	3.70E-06	2.61E-03	1.33E-02	1.89E-05	1.41E-04	312	9.76	-5.46		
8.55E-02	1.01E-10	5.32E-13	1.80E-15	1.72E-01	5.38	4.16E-06	3.38E-03	1.97E-02	2.42E-05	1.83E-04	305	9.76	-5.46		
7.51E-02	1.45E-10	6.78E-13	2.97E-15	1.51E-01	5.33	4.67E-06	4.38E-03	2.91E-02	3.10E-05	2.37E-04	298	9.76	-5.46		
6.62E-02	2.07E-10	8.60E-13	4.88E-15	1.33E-01	5.28	5.24E-06	5.68E-03	4.27E-02	3.94E-05	3.07E-04	291	9.76	-5.46		
5.85E-02	2.95E-10	1.09E-12	8.00E-15	1.17E-01	5.23	5.88E-06	7.36E-03	6.27E-02	5.01E-05	3.98E-04	284	9.76	-5.46		
5.18E-02	4.18E-10	1.37E-12	1.31E-14	1.04E-01	5.18	6.59E-06	9.53E-03	9.16E-02	6.33E-05	5.15E-04	277	9.76	-5.46		
4.61E-02	5.90E-10	1.72E-12	2.12E-14	9.26E-02	5.13	7.39E-06	1.23E-02	1.33E-01	7.98E-05	6.67E-04	270	9.76	-5.46		
4.11E-02	8.28E-10	2.15E-12	3.43E-14	8.26E-02	5.08	8.27E-06	1.60E-02	1.93E-01	1.00E-04	8.64E-04	263	9.77	-5.46		
3.68E-02	1.16E-09	2.67E-12	5.52E-14	7.40E-02	5.03	9.26E-06	2.07E-02	2.80E-01	1.25E-04	1.12E-03	256	9.77	-5.46		
3.31E-02	1.61E-09	3.31E-12	8.85E-14	6.65E-02	4.99	1.03E-05	2.68E-02	4.03E-01	1.56E-04	1.45E-03	249	9.77	-5.46		
2.99E-02	2.23E-09	4.08E-12	1.41E-13	6.00E-02	4.94	1.16E-05	3.46E-02	5.77E-01	1.93E-04	1.87E-03	242	9.78	-5.46		
2.70E-02	3.06E-09	5.00E-12	2.24E-13	5.43E-02	4.89	1.29E-05	4.48E-02	8.24E-01	2.37E-04	2.42E-03	235	9.78	-5.46		
2.46E-02	4.19E-09	6.11E-12	3.54E-13	4.94E-02	4.84	1.44E-05	5.79E-02	1.17E+00	2.91E-04	3.13E-03	228	9.79	-5.46		
2.25E-02	5.69E-09	7.42E-12	5.36E-13	4.51E-02	4.80	1.60E-05	7.49E-02	1.66E+00	3.55E-04	4.05E-03	221	9.80	-5.45		
2.06E-02	7.68E-09	8.96E-12	8.67E-13	4.14E-02	4.75	1.78E-05	9.68E-02	2.34E+00	4.4E-04	5.23E-03	214	9.82	-5.44		
1.90E-02	1.03E-08	1.08E-11	1.35E-12	3.82E-02	4.71	1.98E-05	1.25E-01	3.27E+00	5.19E-04	6.76E-03	207	9.84	-5.43		
1.76E-02	1.37E-08	1.29E-11	2.08E-12	3.53E-02	4.66	2.20E-05	1.61E-01	4.56E+00	6.23E-04	8.73E-03	200	9.87	-5.40		
1.64E-02	1.82E-08	1.53E-11	3.18E-12	3.29E-02	4.61	2.44E-05	2.08E-01	6.33E+00	7.42E-04	1.13E-02	193	9.90	-5.36		
1.53E-02	2.38E-08	1.80E-11	4.84E-12	3.08E-02	4.57	2.71E-05	2.69E-01	8.73E+00	8.79E-04	1.45E-02	186	9.95	-5.30		
1.44E-02	3.10E-08	2.11E-11	7.31E-12	2.90E-02	4.52	3.00E-05	3.47E-01	1.20E+01	1.03E-03	1.88E-02	179	10.01	-5.20		
1.37E-02	4.01E-08	2.54E-11	1.10E-11	2.74E-02	4.48	3.32E-05	4.48E-01	1.67E+01	1.21E-03	2.42E-02	172	10.09	-5.08		
1.30E-02	5.13E-08	2.83E-11	1.63E-11	2.61E-02	4.44	3.66E-05	5.77E-01	2.21E+01	1.40E-03	3.12E-02	165	10.20	-4.82		
1.25E-02	6.50E-08	3.24E-11	2.41E-11	2.50E-02	4.39	4.04E-05	7.43E-01	2.96E+01	1.61E-03	4.02E-02	158	10.34	-4.47		
1.20E-02	8.17E-08	3.68E-11	3.52E-11	2.42E-02	4.35	4.44E-05	9.58E-01	3.95E+01	1.84E-03	5.18E-02	151	10.53	-3.98		
1.17E-02	1.02E-07	4.14E-11	5.11E-11	2.35E-02	4.31	4.89E-05	1.23E+00	5.24E+01	2.08E-03	6.66E-02	144	10.78	-3.28		
1.14E-02	1.25E-07	4.62E-11	7.34E-11	2.28E-02	4.27	5.36E-05	1.59E+00	6.88E+01	2.33E-03	8.58E-02	137	11.10	-2.33		
1.13E-02	1.52E-07	5.11E-11	1.04E-10	2.27E-02	4.23	5.88E-05	2.04E+00	9.87E+01	2.58E-03	1.10E-01	130	11.53	-1.10		
1.12E-02	1.83E-07	5.60E-11	1.47E-10	2.26E-02	4.19	6.43E-05	2.62E+00	1.16E+02	2.84E-03	1.42E-01	123	12.08	0.44		
1.13E-02	2.17E-07	6.06E-11	2.04E-10	2.27E-02	4.15	7.02E-05	3.37E+00	1.48E+02	3.09E-03	1.82E-01	116	12.79	2.26		

(continued)

TABLE II

$\delta^{13}C$ (HCO ₃)		[CO ₂]																							
0.20	12.79	0.06																							
K ₀	K ₁	K ₂	K _{ps}	[H ₂ CO ₃]	pH	[HCO ₃]	Solubility	W/R (C)	X[HCO ₃]	W/R (O)	T °C	$\delta^{18}O_{HCO}$	$\delta^{13}C_{CO}$												
3.58E-01	2.21E-12	4.01E-14	1.01E-17	1.27E+00	5.78	1.68E-06	2.51E-04	1.97E-04	1.32E-06	1.36E-05	375	9.19	-5.69												
3.07E-01	3.28E-12	5.26E-14	1.71E-17	1.09E+00	5.72	1.89E-06	3.26E-04	2.98E-04	1.73E-06	1.76E-05	368	9.19	-5.69												
2.64E-01	4.86E-12	6.87E-14	2.91E-17	9.39E-01	5.67	2.14E-06	4.28E-04	4.50E-04	2.28E-06	2.28E-05	361	9.19	-5.69												
2.28E-01	7.19E-12	8.97E-14	4.92E-17	8.09E-01	5.62	2.41E-06	5.48E-04	6.78E-04	2.98E-06	2.96E-05	354	9.19	-5.69												
1.96E-01	1.06E-11	1.17E-13	8.30E-17	6.98E-01	5.57	2.72E-06	7.12E-04	1.02E-03	3.89E-06	3.85E-05	347	9.19	-5.69												
1.70E-01	1.55E-11	1.51E-13	1.40E-16	6.04E-01	5.51	3.06E-06	9.23E-04	1.53E-03	5.07E-06	4.99E-05	340	9.19	-5.69												
1.47E-01	2.27E-11	1.96E-13	2.34E-16	5.24E-01	5.46	3.45E-06	1.20E-03	2.29E-03	6.59E-06	6.47E-05	333	9.19	-5.69												
1.28E-01	3.32E-11	2.53E-13	3.92E-16	4.55E-01	5.41	3.89E-06	1.55E-03	3.41E-03	8.53E-06	8.39E-05	326	9.19	-5.69												
1.12E-01	4.82E-11	3.25E-13	6.54E-16	3.97E-01	5.36	4.37E-06	2.01E-03	5.07E-03	1.10E-05	1.09E-04	319	9.19	-5.69												
9.76E-02	6.98E-11	4.16E-13	1.09E-15	3.47E-01	5.31	4.92E-06	2.61E-03	7.53E-03	1.42E-05	1.41E-04	312	9.19	-5.69												
8.55E-02	1.01E-10	5.32E-13	1.80E-15	3.04E-01	5.26	5.53E-06	3.38E-03	1.11E-02	1.82E-05	1.83E-04	305	9.19	-5.69												
7.51E-02	1.45E-10	7.18E-13	2.97E-15	2.67E-01	5.21	6.21E-06	4.38E-03	1.64E-02	2.37E-05	2.37E-04	298	9.19	-5.69												
6.62E-02	2.07E-10	8.60E-13	4.88E-15	2.35E-01	5.16	6.97E-06	5.68E-03	2.42E-02	2.97E-05	3.07E-04	291	9.19	-5.69												
5.85E-02	2.95E-10	1.09E-12	8.00E-15	2.08E-01	5.11	7.82E-06	7.36E-03	3.54E-02	3.76E-05	3.95E-04	284	9.19	-5.69												
5.18E-02	4.18E-10	1.37E-12	1.31E-14	1.84E-01	5.06	8.77E-06	9.53E-03	5.17E-02	4.76E-05	5.15E-04	277	9.20	-5.69												
4.61E-02	5.90E-10	1.72E-12	2.12E-14	1.64E-01	5.01	9.83E-06	1.23E-02	7.53E-02	6.00E-05	6.67E-04	270	9.20	-5.69												
4.11E-02	8.28E-10	2.15E-12	3.43E-14	1.46E-01	4.96	1.10E-05	1.60E-02	1.09E-01	7.53E-05	8.64E-04	263	9.20	-5.69												
3.68E-02	1.16E-09	2.67E-12	5.52E-14	1.31E-01	4.91	1.23E-05	2.07E-02	1.58E-01	9.40E-05	1.12E-03	256	9.20	-5.69												
3.31E-02	1.61E-09	3.31E-12	8.85E-14	1.18E-01	4.86	1.38E-05	2.68E-02	2.28E-01	1.17E-04	1.45E-03	249	9.21	-5.69												
2.99E-02	2.23E-09	4.08E-12	1.41E-13	1.06E-01	4.81	1.54E-05	3.46E-02	3.26E-01	1.45E-04	1.87E-03	242	9.21	-5.69												
2.70E-02	3.06E-09	5.00E-12	2.24E-13	9.61E-02	4.77	1.72E-05	4.48E-02	4.66E-01	1.78E-04	2.42E-03	235	9.22	-5.69												
2.46E-02	4.19E-09	6.11E-12	3.54E-13	8.74E-02	4.72	1.91E-05	5.79E-02	6.62E-01	2.19E-04	3.13E-03	228	9.22	-5.69												
2.25E-02	5.69E-09	7.42E-12	5.66E-13	7.93E-02	4.67	2.13E-05	7.49E-02	9.37E-01	2.67E-04	4.05E-03	221	9.24	-5.68												
2.06E-02	7.68E-09	8.96E-12	8.57E-13	7.33E-02	4.62	2.37E-05	9.68E-02	1.32E+00	3.24E-04	5.28E-03	214	9.25	-5.68												
1.90E-02	1.03E-08	1.08E-11	1.35E-12	6.75E-02	4.58	2.64E-05	1.25E-01	1.85E+00	3.91E-04	6.76E-03	207	9.27	-5.67												
1.76E-02	1.37E-08	1.42E-11	2.08E-12	6.25E-02	4.53	2.93E-05	1.61E-01	2.58E+00	4.68E-04	8.73E-03	200	9.30	-5.66												
1.64E-02	1.82E-08	1.53E-11	3.18E-12	5.82E-02	4.49	3.25E-05	2.08E-01	3.58E+00	5.58E-04	1.13E-02	193	9.33	-5.65												
1.53E-02	2.38E-08	1.80E-11	4.84E-12	5.45E-02	4.44	3.60E-05	2.69E-01	4.93E+00	6.61E-04	1.45E-02	186	9.38	-5.62												
1.44E-02	3.10E-08	2.11E-11	7.31E-12	5.13E-02	4.40	3.99E-05	3.47E-01	6.76E+00	7.77E-04	1.88E-02	179	9.44	-5.57												
1.37E-02	4.01E-08	2.45E-11	1.10E-11	4.82E-02	4.36	4.41E-05	4.48E-01	9.21E+00	9.08E-04	2.42E-02	172	9.52	-5.51												
1.30E-02	5.13E-08	2.83E-11	1.63E-11	4.62E-02	4.31	4.87E-05	5.77E-01	1.25E+01	1.05E-03	3.89E-02	165	9.63	-5.41												
1.25E-02	6.50E-08	3.24E-11	2.09E-11	4.45E-02	4.27	5.37E-05	7.43E-01	1.68E+01	1.21E-03	4.02E-02	158	9.77	-5.25												
1.20E-02	8.17E-08	3.68E-11	3.52E-11	4.28E-02	4.23	5.91E-05	9.58E-01	2.24E+01	1.38E-03	5.18E-02	151	9.96	-5.03												
1.17E-02	1.02E-07	4.14E-11	5.11E-11	4.16E-02	4.19	6.50E-05	1.23E+00	2.96E+01	1.56E-03	6.66E-02	144	10.21	-4.71												
1.14E-02	1.25E-07	4.62E-11	7.34E-11	4.07E-02	4.15	7.13E-05	1.59E+00	3.89E+01	1.75E-03	8.58E-02	137	10.54	-4.27												
1.13E-02	1.52E-07	5.11E-11	1.04E-10	4.02E-02	4.11	7.82E-05	2.04E+00	5.07E+01	1.94E-03	1.10E-01	130	10.96	-3.66												
1.12E-02	1.83E-07	5.60E-11	1.47E-10	4.00E-02	4.07	8.55E-05	2.62E+00	6.55E+01	2.14E-03	1.42E-01	123	11.41	-3.03												
1.13E-02	2.17E-07	6.06E-11	2.04E-10	4.01E-02	4.03	9.34E-05	3.37E+00	8.38E+01	2.32E-03	1.82E-01	116	12.22	-1.89												

$\delta^{13}C$ (HCO ₃)		[CO ₂]																							
0.25	12.91	0.08																							
K ₀	K ₁	K ₂	K _{ps}	[H ₂ CO ₃]	pH	[HCO ₃]	Solubility	W/R (C)	X[HCO ₃]	W/R (O)	T °C	$\delta^{18}O_{HCO}$	$\delta^{13}C_{CO}$												
3.58E-01	2.21E-12	4.01E-14	1.01E-17	1.51E+00	5.74	1.82E-06	2.51E-04	1.67E-04	1.21E-06	1.36E-05	375	8.91	-5.80												
3.07E-01	3.28E-12	5.26E-14	1.71E-17	1.29E+00	5.69	2.06E-06	3.26E-04	1.59E-04	1.76E-06	1.76E-05	368	8.91	-5.80												
2.64E-01	4.86E-12	6.87E-14	2.91E-17	1.10E+00	5.63	2.32E-06	4.28E-04	1.91E-04	2.09E-06	2.28E-05	361	8.91	-5.80												
2.28E-01	7.19E-12	8.97E-14	4.92E-17	9.56E-01	5.58	2.62E-06	5.48E-04	5.74E-04	2.74E-06	2.96E-05	354	8.91	-5.80												
1.96E-01	1.06E-11	1.17E-13	8.30E-17	8.25E-01	5.53	2.96E-06	7.12E-04	8.62E-04	3.58E-06	3.85E-05	347	8.91	-5.80												
1.70E-01	1.55E-11	1.51E-13	1.40E-16	7.14E-01	5.48	3.33E-06	9.23E-04	1.29E-03	4.67E-06	4.99E-05	340	8.91	-5.80												
1.47E-01	2.27E-11	1.96E-13	2.34E-16	6.19E-01	5.43	3.75E-06	1.20E-03	1.93E-03	6.06E-06	6.47E-05	333	8.91	-5.80												
1.28E-01	3.32E-11	2.53E-13	3.92E-16	5.38E-01	5.37	4.23E-06	1.55E-03	2.88E-03	7.85E-06	8.39E-05	326	8.91	-5.80												
1.12E-01	4.82E-11	3.25E-13	6.54E-16	4.69E-01	5.32	4.75E-06	2.01E-03	4.29E-03	1.01E-04	1.09E-04	319	8.91	-5.80												
9.76E-02	6.98E-11	4.16E-13	1.09E-15	4.10E-01	5.27	5.35E-06	2.61E-03	6.37E-03	1.30E-05	1.41E-04	312	8.91	-5.80												
8.55E-02	1.01E-10	5.32E-13	1.80E-15	3.59E-01	5.22	6.01E-06	3.38E-03	9.42E-03	1.67E-05	1.83E-04	305	8.91	-5.80												
7.51E-02	1.45E-10	7.18E-13	2.97E-15	3.15E-01	5.17	6.75E-06	4.38E-03	1.39E-02	2.14E-05	2.37E-04	298	8.91	-5.80												
6.62E-02	2.07E-10	8.60E-13	4.88E-15	2.78E-01	5.12	7.58E-06	5.68E-03	2.04E-02	2.73E-05	3.07E-04	291	8.91	-5.80												
5.85E-02	2.95E-10	1.09E-12	8.00E-15	2.46E-01	5.07	8.50E-06	7.36E-03	3.00E-02	3.46E-05	3.98E-04	284	8.91	-5.80												
5.18E-02	4.18E-10	1.37E-12	1.31E-14	2.18E-01	5.02	9.54E-06	9.53E-03	4.38E-02	4.38E-05	5.15E-04	277	8.91	-5.80												
4.61E-02	5.90E-10	1.72E-12	2.12E-14	1.94E-01	4.97	1.07E-05	1.23E-02	6.38E-02	5.52E-05	6.67E-04	270	8.91	-5.80												
4.11E-02	8.28E-10	2.15E-12	3.43E-14	1.73E-01	4.92	1.20E-05	1.60E-02	9.25E-02	6.92E-05	8.64E-04	263	8.91	-5.80												
3.68E-02	1.16E-09	2.67E-12	5.52E-14	1.55E-01	4.87	1.34E-05	2.07E-02	1.34E-01	8.65E-05	1.12E-03	256	8.92	-5.80												
3.31E-02	1.61E-09	3.31E-12	8.85E-14	1.39E-01	4.83	1.50E-05	2.68E-02	1.93E-01	1.08E-04	1.45E-03	249	8.92	-5.80												
2.99E-02	2.23E-09	4.08E-12	1.41E-13	1.25E-01	4.78	1.67E-05	3.46E-02	2.76E-01	1.33E-04	1.87E-03	242	8.93	-5.80												
2.70E-02	3.06E-09	5.00E-12	2.24E-13	1.14E-01	4.73	1.87E-05	4.48E-02	3.94E-01	1.64E-04	2.42E-03	235	8.93	-5.80												
2.46E-02	4.19E-09	6.11E-12	3.54E-13	1.03E-01	4.68	2.08E-05	5.79E-02	5.60E-01	2.01E-04	3.13E-03	228	8.94	-5.80												
2.25E-02	5.69E-09	7.42E-12	5.66E-13	9.44E-02	4.64	2.32E-05	7.49E-02	7.93E-01	2.45E-04	4.05E-03	221	8.95	-5.80												
2.06E-02	7.68E-09	8.96E-12	8.57E-13	8.66E-02	4.59	2.58E-05	9.68E-02	1.12E+00	2.98E-04	5.23E-03	214	8.97	-5.79												
1.90E-02	1.03E-08	1.08E-11	1.35E-12	7.98E-02	4.54	2.87E-05	1.25E-01	1.57E+00	3.59E-04	6.76E-03	207	8.99	-5.79												
1.76E-02	1.37E-08	1.42E-11	2.08E-12	7.39E-02	4.50	3.19E-05	1.61E-01	2.18E+00	4.31E-04	8.73E-03	200	9.01	-5.78												
1.64E-02	1.82E-08	1.53E-11	3.18E-12	6.88E-02	4.45	3.53E-05	2.08E-01	3.03E+00	5.13E																