

Article

Distinct Groups of Low- and High-Fe Ferropericlasite Inclusions in Super-Deep Diamonds: An Example from the Juina Area, Brazil

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Abstract: Diamonds from the Rio Sorriso placer in the Juina area, Mato Grosso State, Brazil, contain mineral inclusions of ferropericlasite associated with MgSiO₃, CaSiO₃, magnesite, merrillite, and other minerals. The ferropericlasite inclusions in Rio Sorriso diamonds are resolved into two distinct genetic and compositional groups: (1) protogenetic, high-Ni and low-Fe (Ni = 8270–10,660 ppm; mg# = 0.756–0.842) ferropericlasites, and (2) syngenetic, low-Ni and high-Fe (Ni = 600–3050 ppm; mg# = 0.477–0.718) ferropericlasites. Based on the crystallographic orientation relationships between natural ferropericlasite inclusions and host diamonds, high-Ni and low-Fe ferropericlasites originate in the upper part of the lower mantle, while low-Ni and high-Fe ferropericlasites, most likely, originate in the lithosphere. Mineral inclusions form the ultramafic lower-mantle (MgSiO₃, which we suggest as bridgmanite, CaSiO₃, which we suggest as CaSi-perovskite, and high-Ni and low-Fe ferropericlasite) and lithospheric (CaSiO₃, which we suggest as breyite, Ca(Si,Ti)O₃, and low-Ni and high-Fe ferropericlasite) associations. The presence of magnesite and merrillite inclusions in association with ferropericlasite confirmed the existence of a deep-seated carbonatitic association. Diamonds hosting high-Ni and low-Ni ferropericlasite have different carbon-isotopic compositions ($\delta^{13}\text{C} = -5.52 \pm 0.75\text{‰}$ versus $-7.07 \pm 1.23\text{‰}$ VPDB, respectively). It implies the carbon-isotopic stratification of the mantle: in the lower mantle, the carbon-isotopic composition tends to become isotopically heavier (less depleted in ¹³C) than in lithospheric diamonds. These regularities may characterize deep-seated diamonds and ferropericlasites not only in the Juina area of Brazil but also in other parts of the world.

Keywords: super-deep diamond; ferropericlasite; merrillite; magnesite; lower mantle; carbon isotopes; carbonatitic association



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1. Introduction

In recent decades, lower-mantle mineral inclusions have been identified in superdeep diamonds from Brazil, Guinea, Canada, South Africa, and Australia [1–9]. These inclusions provide a unique opportunity to establish the actual composition of lower-mantle mineral phases and reveal compositional and structural features of the lower mantle where host diamonds crystallize.

Detailed studies of lower-mantle mineral inclusions in deep-seated diamonds demonstrated the significant features of the lower mantle: its enrichment in Si, the presence of a carbonatitic association, and compositional stratification within the lower mantle ([8] and references therein). However, there are few available samples of diamonds with lower-mantle mineral inclusions, much fewer than Lunar samples, for instance. Each new discovery of lower-mantle material is, therefore, of great importance.

One of the major sources of superdeep diamonds with lower-mantle mineral inclusions is the Juina area in Mato Grosso State, Brazil. A set of oxide mineral inclusions, ferropericlase, CaSiO_3 (former CaSi-perovskite), MgSiO_3 (former bridgmanite), SiO_2 , and others in diamonds from this area, were inferred to originate from depths below 1700 km in [2]. A suggestion on MgSiO_3 as bridgmanite and CaSiO_3 as former CaSi-perovskite was based on their specific compositions (low Al_2O_3 in bridgmanite, for example) and their associations, characteristic for the lower mantle [4]. A few kilometres west of the central Juina area, is the Rio Sorriso (the right tributary of the Rio Aripuana) area, rich in alluvial diamonds. The primary diamond sources in this area are the Pandrea kimberlites, discovered a few kilometres east of the Rio Sorriso. The diamond collection of the Rio Sorriso diamonds was studied earlier by [10], but needed to be completed.

In our previous publications ([8] and references therein), we presented a series of images with intergrowths of these minerals with each other, demonstrating their equilibrium at the time they were formed and incorporated into growing diamonds. The major problem for ferropericlase inclusions in superdeep diamonds is their wide compositional variations from periclase with the magnesium index $mg\# = \text{Mg}/(\text{Mg} + \text{Fe})_{\text{at}}$ at 0.90–0.92 to magnesiowüstite with $mg\# = 0.36$ [8], in some cases even to 0.16 [7], which is close to the end-member wüstite stoichiometry. (For simplicity, we use below the term “ferropericlase” (fPer) for all varieties of the (Fe,Mg)O compositions.) This contradicts experimental data in pyrolitic systems in the pressure range 25–60 GPa, according to which the magnesium index of ferropericlase, in lower-mantle material with $mg\# = 0.80$ –0.95, should be 0.73–0.88 [11,12]. In experiments at pressures up to 100 GPa, for the lower mantle with the most likely magnesium index of $mg\# = 0.89$ –0.92, the magnesium index of coexisting ferropericlase and bridgmanite should be, respectively, at 0.83 and 0.93 just beyond the 660 km discontinuity, and 0.85 and 0.92 at the core–mantle boundary [13]. Further experiments demonstrated that iron-rich ferropericlase (not associated with bridgmanite) forms under lithospheric conditions [14–16]. According to experimental data, CaSiO_3 as breyite may also form under upper mantle conditions [17–19]. That may be the case for single mineral inclusions. However, the association of CaSiO_3 and other minerals with high-pressure minerals like bridgmanite (including touching associations) is good evidence for their lower-mantle origin.

In this work, we presented new data on mineral inclusions in diamonds from the Rio Sorriso placer deposit and offered our interpretation of their origin. For the first time, we also studied the carbon-isotopic compositions of the Rio Sorriso diamonds. Our conclusions on their origin may be applied to not only the Rio Sorriso and Juina areas but also may be crucial for understanding the complex structure of the deep mantle.

2. Materials and Methods

Among the 52 diamonds from the Rio Sorriso studied here, 24 contained 51 mineral inclusions, 29 of which formed non-touching associations in nine samples (Table 1). The diamond crystals were rounded rhombic dodecahedra, as is typical for Brazilian diamonds. The grain sizes varied from 0.1 to 1 mm.

The samples were polished to expose the inclusions. Exposed inclusions were identified in the electron-backscattering mode (BSE). Energy-dispersive spectrometry (EDS) was applied to estimate the composition of inclusions using a focused electron beam (15 kV, 10 nA) and an acquisition time of 30–60 s.

The major elements of minerals were analyzed using a JEOL JXA 8100 electron microprobe. The entire protocol of the X-ray electron probe microanalysis (precision, accuracy, and reference materials) is described in detail in [20]. Quantitative electron probe microanalyses (EPMA) were performed at an accelerating voltage of 15 kV, a sample current of 20 nA, and a beam diameter of 2 μm .

Table 1. Inclusions recovered from Rio Sorriso diamonds.

Minerals and Associations	No of Diamonds	No of Analyzed Inclusions	Sample # *	Association Type
Single grains				
High-Ni ferropericlasite (Ni-fPer)	4	5	1.2.1a, 2.2.1, 2.2.4, 2.7.2a, 3.9.3b	Ultramafic lower-mantle
Low-Ni ferropericlasite (Fe-fPer)	5	10	1.2.1c, 1.2.1d, 1.2.3b, 1.2.3c1, 1.2.3c2, 2.8.2, 2.8.3, 3.6.3a, 3.8.1d, 3.10.1b	Ultramafic lithospheric
Bridgmanite (Brd)	3	3	1.5.2a, <i>F.1</i> , <i>Q.3</i>	Ultramafic lower-mantle
CaSiO ₃	1	1	2.2.2a	Ultramafic lower-mantle, Former CaSiPvk
Merrillite	1	1	3.6.2c	Carbonatitic
Diopside? (Di?)	2	2	2.11.2a, 4.18.1	Lithospheric
Subtotal	16	22		
Associations				
Ni-fPer + Brd	1	6	3.1.3b1, 3.1.3b2, 3.1.3b3, 3.1.b4, 3.1.3b5, 3.1.3b	Ultramafic lower-mantle
fPer + Brd + unidentified	1	3	<i>N3</i>	
Ni-fPer + CaSiO ₃	1	3	2.2.3a, 2.2.3b, 2.2.3c	Ultramafic lower-mantle, Former CaSiPvk
Fe-fPer + CaSiO ₃ + Ca(Si,Ti)O ₃	1	3	1.2.2a, 1.2.2b1, 1.2.2b2	Ultramafic lithospheric
CaSiPvk + Ca(Si,Ti)O ₃	1	2	<i>Q2</i>	Lithospheric
fPer + Magnesioferrite	1	3	<i>F3</i>	Ultramafic
Fe-fPer + Magnesite	1	3	1.2.4b, 1.2.4d, 1.2.4c	Carbonatitic
Fe-fPer + Merrillite	1	6	3.10.1a	Carbonatitic
Subtotal	8	29		
Total	24	51		

Note: * The samples indicated in *italics* are partly analyzed.

Raman spectra were collected using a Horiba Jobin Yvon LabRAM HR800 Raman microspectrometer equipped with a 532 nm Nd:YAG laser and an Olympus BX41 microscope at $\times 50$ magnification. Spectra were recorded at room temperature in a backscattering geometry in the range of 100 to 1200 cm^{-1} with a spectral resolution of approximately 1 cm^{-1} . The spectra were calibrated using the 520.6 cm^{-1} line of a silicon wafer. The wavenumbers were accurate to $\pm 1 \text{ cm}^{-1}$.

The carbon-isotopic ratios were measured using a Flash EA 1112 (Thermo Fisher Scientific, Waltham, MA, USA) coupled to a Finnigan Delta Plus XP isotope-ratio mass spectrometer. The diamonds were crushed in an agate mortar, and diamond fragments of approximately 50–100 μm were inserted into Sn capsules and dropped into the combustion reactor (1020 $^{\circ}\text{C}$). The temperature of the reduction reactor was maintained at 650 $^{\circ}\text{C}$. All carbon-isotopic compositions of the samples are reported in standard δ notation in the Vienna Pee Dee Belemnite Reference standard (VPDB) scale ($\delta^{13}\text{C}_{\text{VPDB}}$). Two to nine fragments of each sample were analyzed to calculate the average and deviation (1σ) values.

To prevent bias and to minimize error, the accuracy of the isotopic data was evaluated by analyzing the certified reference material NBS 22 (oil with $\delta^{13}\text{C} = -30.03 \pm 0.04\text{‰}$) obtained from the International Atomic Energy Agency, Vienna, Austria). High-purity helium ($>99.9999\%$; from NIIKM) and CO_2 ($\geq 99.999\%$; Voessen, Moscow, Russia) were used as carrier gas or working standard gas, respectively. The maximum standard deviation (STD) for $\delta^{13}\text{C}$ analysis of reference material was 0.15 ‰ .

3. Results

Most of the inclusions were ferropericlasite, including 15 single grains and 12 grains in association with MgSiO_3 (which we suggest as retrogressed bridgmanite, see below), CaSi - and $\text{Ca}(\text{Si,Ti})$ -perovskites, magnesioferrite, magnesite, and merrillite. Ferropericlasite formed octahedral and cuboctahedral, sometimes elongated and flattened crystals (Figure 1).

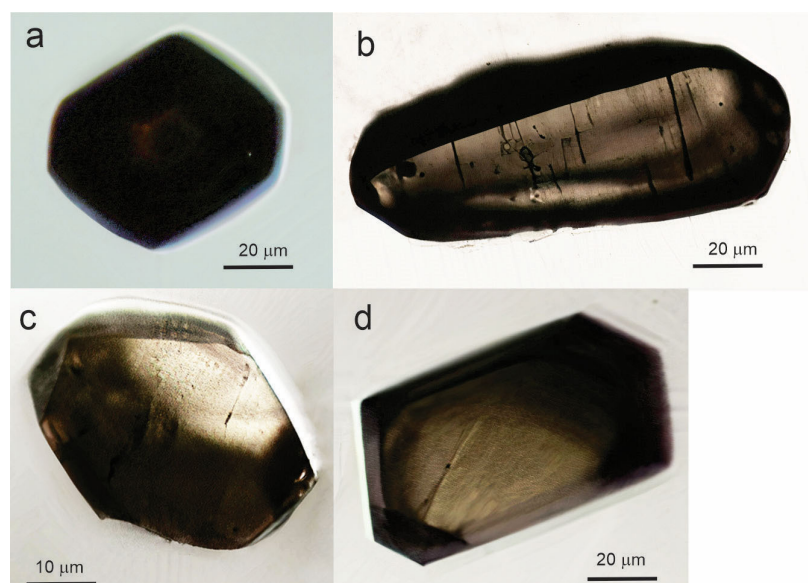


Figure 1. Crystals of ferropericlase included in the Rio Sorriso diamonds. (a) Sample #2.2.1. (b) Sample #3.1.3b. (c) Sample #3.1.3c (all high-Ni and low-Fe). (d) Sample #3.6.3a (low-Ni and high-Fe).

Magnesite and merrillite were identified in three diamonds. This was the first time these minerals were found in superdeep diamonds in association with ferropericlase. Merrillite was identified in the terrestrial environment for the first time [21]. In addition, eclogitic garnet and two grains of diopside composition were identified in three diamonds. The composition of the mineral inclusions identified in the studied diamonds is presented in Tables 2 and S1.

Table 2. Representative chemical analyses of oxide inclusions in studied diamonds from the Rio Sorriso (wt.%).

Sample	3.1.3b1	2.2.3a	1.2.2a	3.10.1a	3.1.3b	2.2.3a	1.2.2b
Mineral	Ni-fPer	Ni-fPer	Fe-fPer	Fe-fPer	Brd	CaSiO ₃	CaSiTiO ₃
Association	Ni-fPer+ Brd	Ni-fPer+ CaSiO ₃	Fe-fPer+ CaSiO ₃ +CaSiTiO ₃	Fe-fPer+ Merrill	Ni-fPer+ Brd	Ni-fPer+ CaSiPrv	Fe-fPer+ CaSiO ₃ + CaSiTiO ₃
SiO ₂	0.02	0.06	0.05	0.01	56.32	51.58	12.92
TiO ₂	0.01	0.01	0.02	0.01	0.12	0.04	40.28
Al ₂ O ₃	0.15	0.04	0.04	0.12	1.26	0.09	1.83
Cr ₂ O ₃	0.75	0.53	0.16	1.21	0.08	0.01	1.33
FeO	33.74	35.88	59.06	62.86	4.91	0.28	0.51
NiO	1.11	1.18	0.22	0.10	0.01	0.02	n.a.
MnO	0.49	0.29	0.37	1.47	0.11	0.03	n.a.
MgO	62.29	60.52	38.44	32.19	35.32	n.a.	n.a.
CaO	0.00	n.a.	n.a.	0.01	0.10	47.44	38.06
Na ₂ O	0.61	0.21	0.09	1.43	0.07	0.06	n.a.
K ₂ O	0.00	0.01	n.a.	n.a.	0.02	0.02	n.a.
Total	99.18	98.72	98.45	99.41	98.31	99.56	94.93
<i>fe#</i>	0.233	0.249	0.463	0.523	0.072	—	—
<i>mg#</i>	0.767	0.751	0.537	0.477	0.928	—	—

Note: n.a.—not analyzed.

3.1. Inclusions of Ferropericlasite

Like elsewhere in Brazil and also in Guinea and Canada ([1,3,4,7], and others), ferropericlasite inclusions in the Rio Sorriso diamonds have very variable iron content, from 24.6 to 62.9 wt.% FeO, and $mg\#$ values of 0.477–0.842 (Figure 2). The great variation in the composition of ferropericlasite, with $mg\#$ values between 0.36 and 0.92 (that is even more variable than the $mg\#$ values of the ferropericlasite grains studied here), was established in earlier works ([8,10] and references therein). In the studied ferropericlasite samples, the $mg\#$ values demonstrated a bimodal distribution with two maxima: at 0.596 (variation from 0.477 to 0.718) and 0.790 (variation from 0.756 to 0.842) (Figure 2).

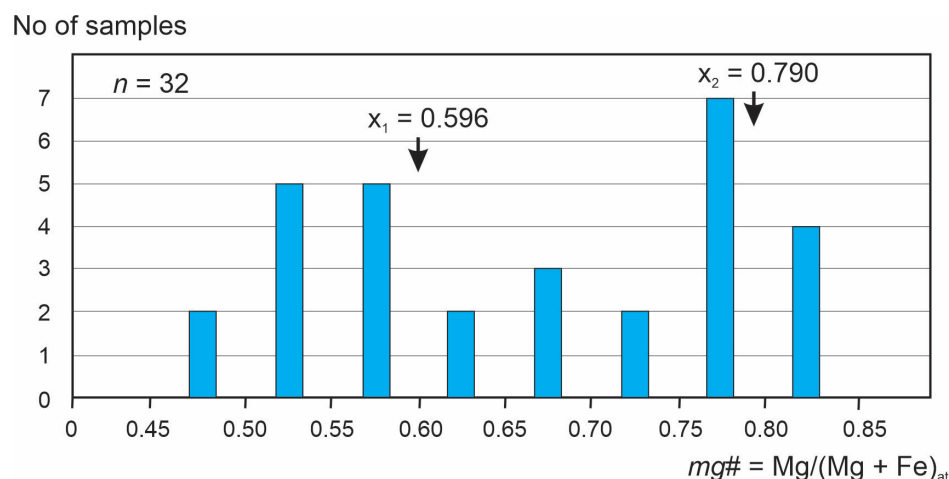


Figure 2. Distribution of the Mg index ($mg\#$) in ferropericlasite grains. The arrows indicate the positions of average $mg\#$ values for two groups of ferropericlasite.

The two ferropericlasite groups differed not only in their $mg\#$ values but also in their Ni contents. Ferropericlasite of the first group (low-Fe, high-Ni) contained 8270–10,660 ppm Ni, while that of the second group (high-Fe, low-Ni) contained 600–3050 ppm Ni (Figure 3). In one of the samples (#1.2.1), low-Fe, high-Ni ($mg\# = 0.769$) and high-Fe, Ni-poor ($mg\# = 0.566$ – 0.567) ferropericlasite inclusions coexisted (Table S1).

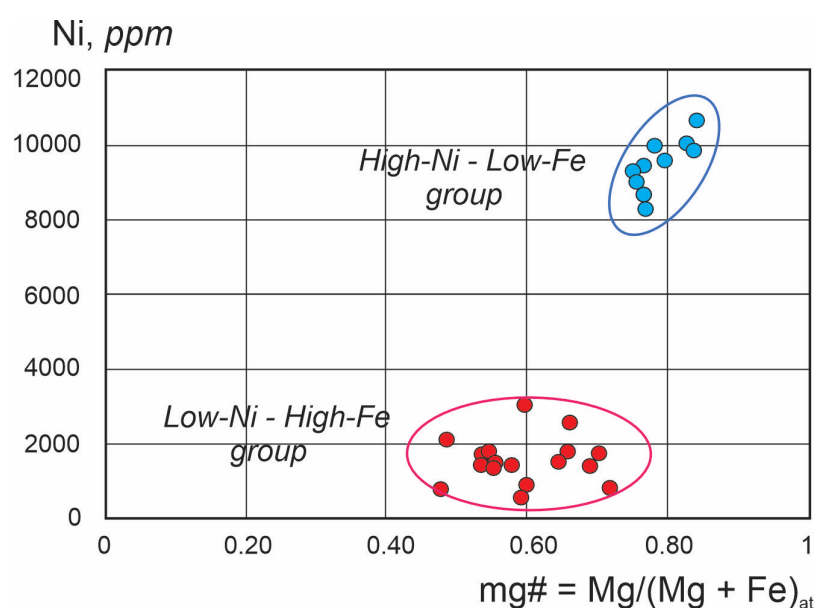


Figure 3. Ni content vs. Mg index ($mg\#$) in ferropericlasite grains.

In several samples, ferropericlase associates with MgSiO_3 (which we suggest former bridgmanite; see below in Section 3.2), CaSiO_3 and $\text{Ca}(\text{Si,Ti})\text{O}_3$, magnesioferrite, magnesite, and merrillite. MgSiO_3 and CaSiO_3 associate with low-Fe, high-Ni ferropericlase (the first group), magnesite, and merrillite associate with high-Fe, Ni-poor ferropericlase (the second group). In sample #1.2.2, where CaSiO_3 associates with $\text{Ca}(\text{Si,Ti})\text{O}_3$, ferropericlase was also high-Fe, Ni-poor.

3.2. Other Mineral Inclusions

The analyzed grains of MgSiO_3 (samples #1.5.2a and #3.1.3b; the latter associated with high-Ni–low Fe ferropericlase; Table S1) have high Mg index values ($mg\# = 0.911\text{--}0.928$), low Al ($\text{Al}_2\text{O}_3 = 1.26\text{--}2.25$ wt.%), and very low Ni ($0\text{--}0.01$ wt.%) contents, characteristic of the lower-mantle ultramafic association [8]. The very low Ni contents in the MgSiO_3 phase are specific for former bridgmanite. Ferropericlase, with which MgSiO_3 associates in sample #3.1.3, was high-Ni–low-Fe variety with $mg\# = 0.767\text{--}0.841$. These Mg indices correspond precisely to the $mg\#$ values in coexisting ferropericlase and bridgmanite crystallized in experiments modelling the lower-mantle conditions beyond the 660 km discontinuity [12,13]. This gives the reason to consider the observed MgSiO_3 inclusions as former *bridgmanite*.

The identification of CaSiO_3 inclusions is more complex. Based on their low Al content ($\text{Al}_2\text{O}_3 = 0.06\text{--}0.59$ wt.%), all studied CaSiO_3 grains belong to the ultramafic association [8]. In the absence of structural data, they may be *CaSi-perovskite* (“davemaite” [22–24]) or low-pressure breyite, which crystallizes at lithospheric conditions or forms as a retrograde phase of *CaSi-perovskite* at 9–10 GPa (e.g., [25]). In our samples, CaSiO_3 grains associate with both types of ferropericlase, low-Fe and high-Ni (the first group, sample #2.2.3) and high-Fe and Ni-poor ferropericlase (the second group, sample #1.2.2) (Table S1). In the latter sample, high-Fe and Ni-poor ferropericlase associated not only with CaSiO_3 but also with $\text{Ca}(\text{Si,Ti})\text{O}_3$. We suggest that both CaSiO_3 mineral phases occur in the studied diamonds, former *CaSi-perovskite* (sample #2.2.3) and *breyite* (sample #1.2.2).

The grain of *Ca(Si,Ti)O₃-perovskite* with 40.28 wt.% TiO_2 , 12.92 wt.% SiO_2 , and minor Al_2O_3 (1.83 wt.%), Cr_2O_3 (1.33 wt.%) and FeO (0.51 wt.%) (Table S1, sample #1.2.2b2) occurred in association with low-Ni and high-Fe ferropericlase (sample #1.2.2a) and suggests lithospheric origin. Like CaSiO_3 in sample #2.2.3, it also had low Al (0.05 wt.% Al_2O_3) and may be attributed to the ultramafic association; the association with low-Ni ferropericlase suggests a possible breyite.

$\text{CaSiO}_3 + \text{Ca}(\text{Si,Ti})\text{O}_3$ inclusions were previously identified in diamonds from the Juina-5 kimberlite pipe [26] and Sao Luis alluvial deposits, also in the Juina area [7,27]. Two of these grains contained a significant amount of Si, like in our sample (11.00–12.05 wt.% SiO_2). One of the $\text{Ca}(\text{Si,Ti})\text{O}_3$ inclusions with relatively low Ti (6.65 wt.% TiO_2 ; #13 in [7]) associates with former bridgmanite and may have attributed to the lower mantle.

Magnesite, as a member of the deep-seated natrocarbonatitic association, was identified earlier as inclusion in diamond in association with other carbonates (dolomite, eitelite), halides (halite, sylvite), sulfides (pentlandite, violarite), native Fe^0 , and an unnamed phosphate $\text{Na}_4\text{Mg}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ [8]. In the studied sample set, magnesite, in touching association with low-Ni ferropericlase in diamond #1.2.4 (Figure 4a), was confirmed by Raman spectroscopy (Figure 4b). It was almost pure MgCO_3 with minor admixtures of Fe (2.76 wt.% FeO), Mn (0.12 wt.% MnO), Ca (1.29 wt.% CaO), and Na (0.06 wt.% Na_2O). It had the empirical formula $(\text{Mg}_{0.94}\text{Fe}_{0.04}\text{Ca}_{0.02})\text{CO}_3$. This was the first find of magnesite as intergrowth with ferropericlase. The admixture of Na in this sample points to its natrocarbonatitic association.

Merrillite $\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_{14}$, earlier described as β -tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ [21], was identified in two Rio Sorriso samples: #3.6.2 and #3.10.2. In sample #3.6.2, merrillite occurred as a single elongate inclusion, approximately 40 μm in size. In sample #3.10.2, merrillite formed a chain of five tabular, elongate inclusions, each 15–50 μm in size (Figure 5), in association with ferropericlase with $mg = \text{Mg}/(\text{Fe} + \text{Mg})_{\text{at}} = 0.477$

and low-Ni (NiO = 0.10 wt.%). The composition of merrillite from sample #3.10.2 was (from four analyses, in wt.%): 0.02–0.05 SiO₂, 0–0.08 TiO₂, 0.02–0.10 Al₂O₃, 0–0.02 Cr₂O₃, 1.19–2.07 FeO, 0.01 NiO, 0.08–0.12 MnO, 0–2.95 MgO, 46.4–48.4 CaO, 1.61 SrO, 0.08–1.92 Na₂O, 0.04–0.63 K₂O, 43.9–44.2 P₂O₅, 2.03 SO₃ [21]. This gives the empirical formula of the found merrillite as Ca_{18.85}Sr_{0.36}Na_{1.44}K_{0.32}Fe_{0.39}P_{14.07}S_{0.57}O_{56.00} (average of four analyses) on the basis of 56 oxygen atoms per formula. This composition differs from the known Lunar samples, in which Mg >> Fe [28], although in sample #3.6.2 MgO = 2.95 wt.%, and is closer to Martian ferromerrillite [29]. The Raman spectra of these merrillite grains are presented in Figure 6. There were several vibrations with modes at 407, 960, 973, and 1080 cm^{−1} from sample no. 3.6.2, and 217, 404, 443, 473, 607, 965, 970, and 1065 cm^{−1} from sample no. 3.10.2. These mode energies correspond almost exactly to the Raman shifts of merrillite from the Suizhou meteorite [30]. Based on these data, the structure of the found merrillite was trigonal with the *R3-m* space group [21]. Like other phosphates previously identified in diamonds from the Juina area, merrillite may be attributed to the carbonatitic association alongside magnesite.

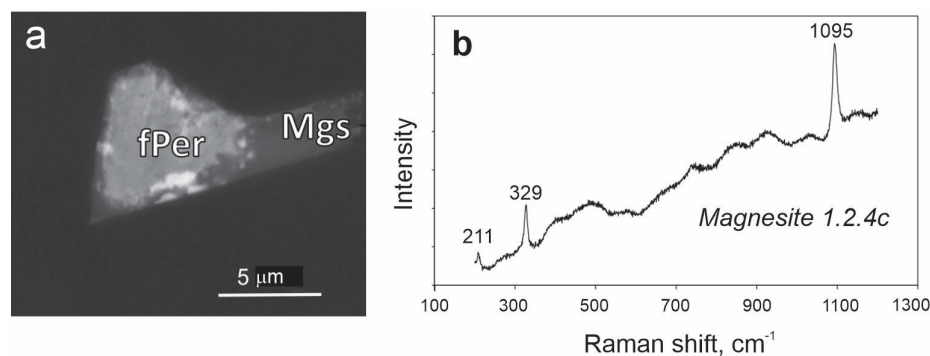


Figure 4. Magnesite in touching association with ferropericlase included in Rio Sorriso diamond #1.2.4. (a)—Electronic image. (b)—Its Raman spectrum.

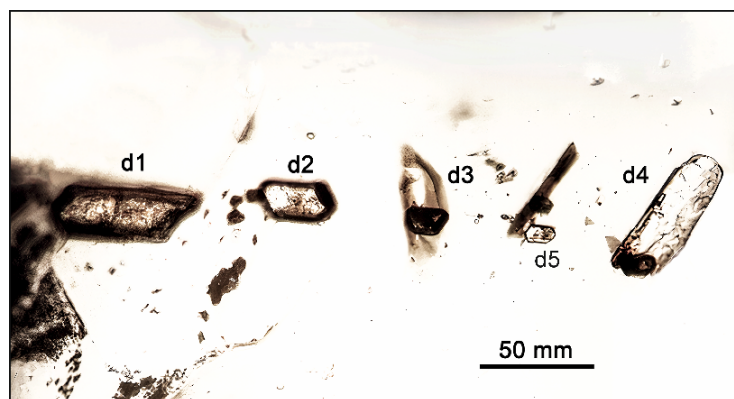


Figure 5. Inclusions of merrillite in diamond #3.10.2 from the Rio Sorriso area. From [21], with permission from the Mineralogical Society of America.

Three diamonds from the studied ones contained *upper-mantle mineral grains*. Eclogitic-type garnet was identified in sample #F2, and two grains of CaMgSi₂O₆, compositionally corresponding to diopside, were identified in samples #2.11.2 and #4.18.1. It is thus possible that, like the Guinean [31] and Canadian [5] deposits, the Rio Sorriso placer contains upper-mantle diamonds alongside lower-mantle ones.

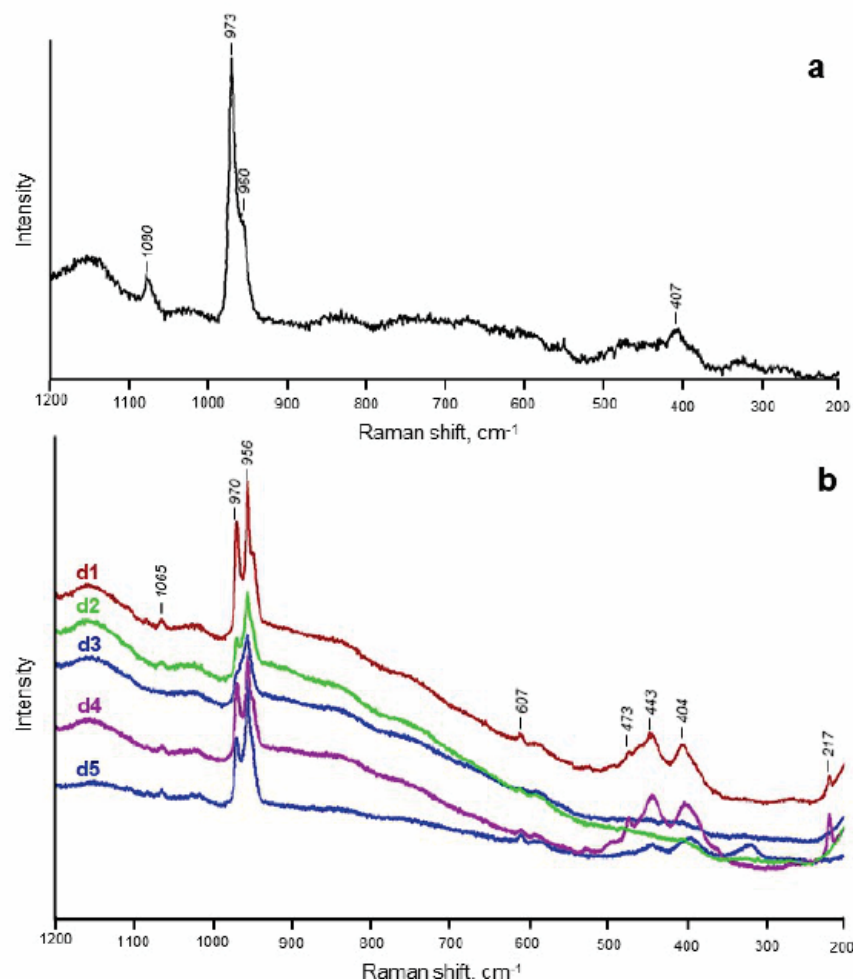


Figure 6. Raman spectra of merrillite. (a) From sample 3.6.2. (b) From sample 3.10.2. From [21], with permission from the Mineralogical Society of America.

3.3. Carbon-Isotope Composition

The carbon-isotope values ($\delta^{13}\text{C}$) of 53 analyzed Rio Sorriso diamonds ranged from -3.64 to -8.94% VPDB (Tables 3 and S2). Intra-sample variations were small, with $\Delta = 1\text{--}3\%$ VPDB and deviations less or slightly exceeding 1% VPDB, which is characteristic of most natural diamonds. Still, in the 1980s, we demonstrated that most diamonds have intra-sample $\delta^{13}\text{C}$ variations at $\pm 2\%$ PDB and some at $5\text{--}10\%$ PDB [32]. Since then, dozens of SIMS analyses have shown intra-sample variations caused by diamond zonation up to $10\text{--}14\%$. Only one sample (#6.3.1) had $\delta^{13}\text{C} = -11.41 \pm 2.10\%$ VPDB. In this sample, $\delta^{13}\text{C}$ values varied from -9.58% to -15.03% VPDB ($\Delta = 5.45\%$ VPDB) between various diamond fragments. This is caused, most likely, by the zonation of the crystal and varying carbon isotopic compositions in different crystal zones during the diamond growth. Diamond #6.3.1 may not belong to the deep mantle population. All the other diamonds in the sample set have a more homogeneous carbon-isotopic composition ($\Delta = 1\text{--}3\%$ VPDB).

Of particular interest were carbon-isotopic compositions of diamonds enclosing distinct, high-Ni (low-Fe) and low-Ni (high-Fe) ferropericlases. The diamond hosts of each of these ferropericlase groups had different $\delta^{13}\text{C}_{\text{VPDB}}$ values: $-5.52 \pm 0.75\%$ for diamonds with high-Ni, low-Fe ferropericlase; and $-7.07 \pm 1.23\%$ for those with low-Ni, high-Fe ferropericlase (Tables 3 and S2, Figure 7). The results of Student's *t*-test, performed with the use of the SigmaPlot12 software, demonstrated that for the two diamond groups with 13 degrees of freedom and a 95% coefficient confidence interval, the difference of means was 0.451 to 2.643. The difference in the mean values of the two groups (-5.52% and -7.07%) was greater than would be expected by chance; there was a statistically significant

difference between the two groups ($P = 0.009$). A non-parametric Mann–Whitney U -test also confirmed the statistical difference between $\delta^{13}\text{C}$ values for the two diamond groups with a 95% confidence: the U -value for them was 4, while a critical value at $P < 0.05$ was 8, and the z -score was 2.5103 with the p -value 0.01208.

Table 3. Carbon-isotopic composition in Rio Sorriso diamonds with ferropericlasite inclusions.

Sample	No of Anal.	$\delta^{13}\text{C}_{\text{VPDB}}, \text{‰}$		Ni in fPer, ppm
		Average	St. Deviation	
With high-Ni ferropericlasite inclusions				
1.2.1	3	−5.53	0.38	8275
2.2.1	5	−5.60	0.59	9053
2.2.3	4	−5.61	0.74	9288
2.2.4	5	−5.20	0.14	9438
2.7.2	3	−5.93	1.08	9595
3.2.2	9	−6.44	0.81	9862
3.5.2	8	−5.50	0.83	10,023
3.9.3	5	−6.15	0.27	9980
3.10.2	5	−5.59	0.45	9037
N	5	−3.64	0.71	9172
Average		−5.52	0.75	
With low-Ni ferropericlasite inclusions				
1.2.2	3	−5.76	0.90	1537
1.2.3	6	−8.94	1.34	1709
2.8.3	3	−6.37	0.60	1737
3.6.3	2	−7.56	0.87	1784
3.10.1	3	−6.70	0.17	1466
Average		−7.07	1.23	

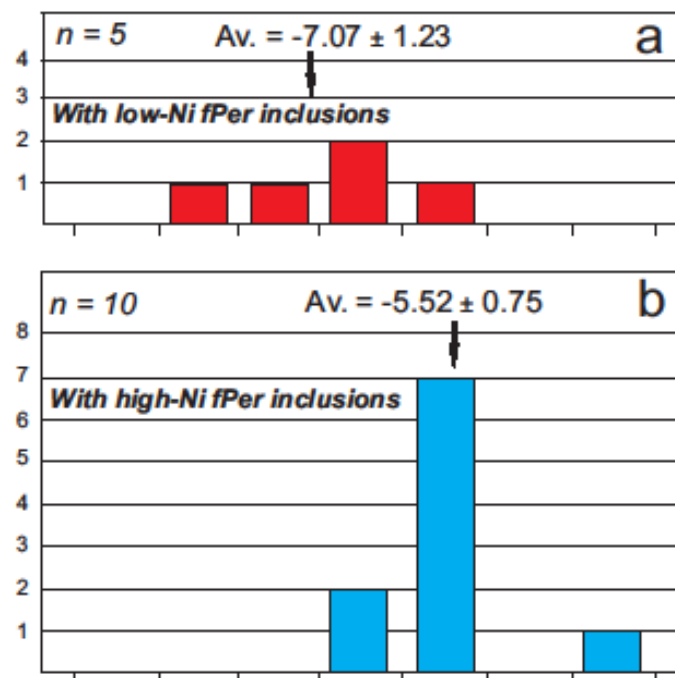


Figure 7. Cont.

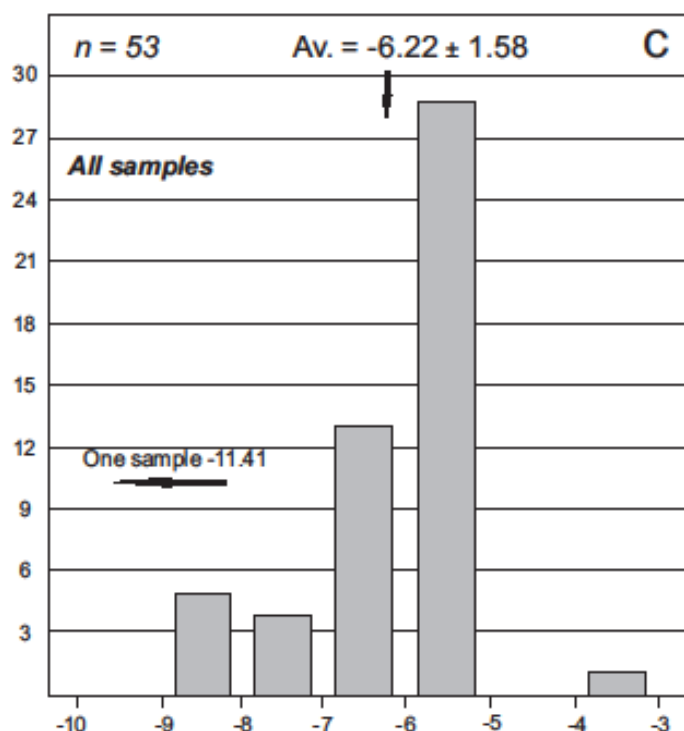


Figure 7. Carbon isotopic composition in Rio Sorriso diamonds. (a) With low-Ni and high-Fe ferropericase inclusions. (b) With high-Ni and low-Fe ferropericase inclusions. (c) All diamonds studied.

4. Discussion

The distinguished *two separate groups of ferropericase* have different compositions, different carbon-isotope characteristics of the host diamonds, and different mineral associations. The first group, high-Mg (low-Fe), contained 8270–10,660 ppm Ni, while the second group, low-Mg (high-Fe) ferropericase, contained significantly less, 600–3050 ppm Ni (Figure 3). The high-Ni and low-Fe ferropericases of the first group associated with former bridgmanite and former CaSi-perovskite (“davemaoite”) from the lower mantle (Table 1), which means its lower-mantle origin as well. As established by Frost et al. [33], the Ni content in ferropericase was an indicator of the metal Fe phase(s) in the magmatic system of the deep mantle. An increase in the fraction of the metallic phase led to a decrease in the Ni concentration in the lower-mantle material and, consequently, to a decrease in the Ni content in ferropericase. According to experimental data [34], the concentration of Ni in the lower mantle before the release of a metallic alloy is estimated to be 1 wt.% (10,000 ppm), similar to the Ni content of Mg-rich (low-Fe) ferropericase in our sample set (Figure 3). Thus, a high-Ni and low-Fe and Mg-rich ferropericase was formed in a medium that contained little metallic alloy, probably within the uppermost lower mantle.

It was suggested that Mg-rich ferropericases mainly represent ambient lower mantle trapped as protogenetic inclusions, while Fe-rich ferropericases, syngenetic with host diamonds, indicate redox growth in the upper mantle [35]. Earlier, based on the Fe partitioning between bridgmanite and ferropericase, we proposed that the Fe content increases with depth (pressure), reflecting a higher Fe content in the deeper part of the lower mantle [36]. However, in that correlation, all ferropericases associated with bridgmanite were high-Ni, high-Mg, and low-Fe varieties, and that conclusion may be applied only to the first group ferropericases.

Fe-rich, Ni-poor ferropericase inclusions of the second group are too iron-rich to have equilibrated as part of an assemblage associated with primitive mantle peridotite or harzburgite [9]. Several experimental works demonstrated that they might originate within shallower Earth’s layers, upper mantle, and or transition zone [16–18]. The analysis of crystallographic orientation relationships between natural ferropericase inclusions and

host diamonds confirmed these data. It demonstrated that Mg-rich ferropericlasite grains were trapped by growing diamonds within the lower mantle, and Fe-rich ferropericlasites are syngenetic with their host diamonds and form under redox growth in the upper mantle [37]. The low-Ni and high-Fe ferropericlasites do not associate with former bridgmanite and former CaSi-perovskite (“davemaoite”) but with Ca(Si,Ti)O₃, magnesite, and merrillite.

These facts indicate that, in one locality, two distinct groups of ferropericlasite inclusions and, possibly, two generations of the host diamonds may occur. Ferropericlasite grains with high *mg#* (0.756–0.842) and high Ni content (8270–10,660 ppm), associated with low-Al MgSiO₃ (which we suggest former bridgmanite) (Al₂O₃ = 1.26 wt.%; sample #3.1.3) and CaSiO₃ (which we suggest former CaSi-perovskite) (samples #2.2.1 and 2.2.3), originated from the upper parts of the lower mantle. Low-*mg#* (0.477–0.718) and low-Ni (600–3050 ppm) ferropericlasites originated from the upper mantle and/or transition zone. In sample #1.2.1, one low-Fe, high-Ni and two high-Fe, Ni-poor ferropericlasite inclusions were found to coexist. To our knowledge, such an association was never observed before in natural samples and was never obtained in experiments. The coexistence of compositionally different ferropericlasite grains in the same diamond, as well as by variable carbon isotopic composition in diamond #1.2 (from $-5.53 \pm 0.38\%$ to $-8.94 \pm 1.34\%$ Table S2), suggests that diamond #1.2 grew under changing conditions. This does not necessarily mean that these diamonds formed at great depths, ascending through the mantle in a plume and then grew again at shallower depths through different processes and under different conditions. The observed chemical disequilibrium may rather reflect progressive chemical mass transfer during a reaction between a fluid released by a deeply subducted mafic slab with ambient peridotite [35,38].

Magnesioferrite was found as a single grain #F3 in association with ferropericlasite. Earlier, magnesioferrite was identified as microcrystals in ferropericlasite formed as an exsolution phase in Ni-rich ferropericlasite grains [35]. It was suggested that the appearance of magnesioferrite in such a position results by the oxidation of ferropericlasite caused by the intrusion of subducted material into the sublithospheric mantle [35]. To the best of our knowledge, magnesioferrite in this study is the first find as a single grain.

Magnesite was found, in sample #1.2.4, in association with Ni-poor and Fe-rich ferropericlasite (Figure 4). In this case, ferropericlasite might also crystallize as a product of redox reactions involving oxidized carbonate or carbonated melt and reducing peridotite at the upper mantle, the transition zone or the lower mantle conditions [9].

Merrillite was known earlier only in meteorites and Lunar rocks. Recently, a Na-poor analogue of merrillite, keplerite Ca₉(Ca_{0.5} Mg_{0.5})Mg(PO₄)₇ with an *R3c* space group was described from the Marjalahati meteorite; it was suggested as an indicator of high-temperature environments characterized by extreme depletion of Na [39]. Among the studied Rio Sorriso diamonds, we found two samples with merrillite inclusions [21]. In these diamonds, the $\delta^{13}\text{C}_{\text{VPDB}}$ values were $-5.56 \pm 0.54\%$ (sample #3.6.2) and $-5.59 \pm 0.45\%$ (sample #3.10.2),—characteristic to deep juvenile carbon composition. In sample #3.10.1, merrillite associates with low-Ni and high-Fe ferropericlasite and, like magnesite, may be attributed to the carbonatitic association, along with other phosphates identified as inclusions in diamond. We suggest that merrillite from the studied diamonds may be a retrograde phase of tuite, a high-pressure modification of tricalcium phosphate ($\gamma\text{-Ca}_3(\text{PO}_4)_2$) [21].

Identifying both minerals, magnesite and merrillite, as inclusion in diamonds in association with ferropericlasite is additional evidence for the existence of a carbonatitic association in the deep mantle and the participation of carbonates in the formation of diamonds [40]. Experiments demonstrated that Fe-rich, Ni-poor ferropericlasite might form by reacting mantle peridotite with carbonate melt at pressure conditions, corresponding to the deep upper mantle and transition zone [16,17]. These experiments explain why Fe-rich, Ni-poor ferropericlasite is not associated with bridgmanite but often with *carbonatitic minerals*.

All studied diamonds have *carbon isotopic composition* $\delta^{13}\text{C}_{\text{VPDB}}$ between -3.64 and -8.94% (except for #6.3.1 with $\delta^{13}\text{C}_{\text{VPDB}} = -11.41 \pm 2.10\%$). This corresponds to the $\delta^{13}\text{C}_{\text{VPDB}}$ “juvenile” values of diamonds of the ultramafic association [41]. The $\delta^{13}\text{C}_{\text{VPDB}}$

values in diamonds with inclusions support the distinction between the two groups of ferropericlasite. Diamonds with high-Ni, low-Fe ferropericlasite inclusions from the lower mantle have $\delta^{13}\text{C}_{\text{VPDB}} = -5.52 \pm 0.75\text{‰}$ —notably heavier than the $\delta^{13}\text{C}$ values in diamonds with low-Ni (high-Fe) ferropericlasite inclusions from the upper mantle or the transition zone with $\delta^{13}\text{C}_{\text{VPDB}} = -7.07 \pm 1.23\text{‰}$ (Supplementary Table S2, Figure 5). The difference between the two groups is statistically significant with 95% coefficient confidence interval, according to the Student *t*-test and the Mann–Whitney *U*-test. This difference in $\delta^{13}\text{C}$ values reflects a possible stratification in the carbon-isotopic composition of the lower mantle. Accepting the origin of high-Ni, low-Fe ferropericlasite in the lower mantle, it may be suggested that, in the lower mantle, the carbon-isotopic composition tends to become isotopically heavier (less depleted in ^{13}C) than in the lithospheric diamonds. This conclusion is preliminary substantiated only for the Juina area so far and needs to be checked for other regions. More data are needed to substantiate the proposed hypothesis.

5. Conclusions

New finds of mineral inclusions in lower-mantle diamonds from the Rio Sorriso, Juina area, Brazil, allow the following conclusions to be drawn.

1. In the Rio Sorriso diamonds, the ferropericlasite inclusions are resolved into two distinct genetic and compositional groups: (1) a protogenetic, high-Ni and low-Fe group, and (2) a syngenetic, low-Ni and high-Fe group. High-Ni and low-Fe ferropericlasites originate in the upper part of the lower mantle, while low-Ni and high-Fe ferropericlasites, most likely, originate within the upper mantle or the Earth's transition zone.
2. Mineral inclusions in the Rio Sorriso diamonds form the ultramafic lower-mantle (MgSiO_3 , which we suggest as bridgmanite, CaSiO_3 , which we suggest as CaSi -perovskite, and high-Ni and low-Fe ferropericlasite) and lithospheric (CaSiO_3 , which we suggest as breyite, $\text{Ca}(\text{Si,Ti})\text{O}_3$, and low-Ni and high-Fe ferropericlasite) associations. Minerals of the carbonatitic association as inclusions in diamonds (magnesite and merrillite) also occur.
3. The diamond hosts of each ferropericlasite group have different carbon-isotopic compositions, indicating that diamonds become isotopically heavier with depth ($\delta^{13}\text{C}_{\text{VPDB}} = -5.52 \pm 1.23\text{‰}$ in the lower mantle versus $-7.07 \pm 0.75\text{‰}$ in the upper mantle or transition zone).

These regularities may characterize deep-seated diamonds and ferropericlasites not only in the Juina area of Brazil but also in other parts of the world. Subsequent studies of ferropericlasite inclusions in super-deep diamonds should be performed.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13091217/s1>, Table S1: Chemical compositions of oxide, carbonate and silicate(?) inclusions in the studied lower-mantle diamonds from Rio Soriso, Table S2: Isotopic composition of carbon in diamonds from Rio Soriso.

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