

Uranium irradiation history of carbonado diamond; implications for Paleoproterozoic oxidation in the São Francisco craton

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ABSTRACT

Carbonado is a porous polycrystalline diamond rock found in central African and Brazilian placer deposits. It contains unsupported radiogenic isotopes of He, Ne, Kr, Xe, and Pb. Here we show that these, and the radiation-related defects introduced to the diamond structure, are a result of uranium precipitation, with no isotopic or spectroscopic evidence of Th enrichment. The daughter products are unsupported due to Proterozoic U remobilization. Combining existing carbonado Pb isotope data with recent studies of the geochronology of the tectonic evolution of the São Francisco craton (eastern South America) reveals that the most likely scenario is Paleoproterozoic uranium enrichment of carbonado, followed by Mesoproterozoic uranium dissolution. Under all possible scenarios, the carbonado radiation damage history requires U mobilization in the Mesoarchean or late Paleoproterozoic. This is consistent with recent studies of South Africa and India Mesoarchean paleosols, which also show evidence for local oxygen activity greater than that of the Archean atmosphere and ocean. While those studies rely on whole-rock trace element and transition metal stable isotope measurements, this combination of crystallographic defects, sedimentary geochronology, and radiogenic isotopes supports the same conclusions of nonmarine, near-surface Archean oxygen enhancement.

INTRODUCTION

Carbonado Irradiation Evidence

Carbonado is a gravel- to cobble-sized, porous, polycrystalline diamond aggregate found in placer deposits in Brazil and Central African Republic. Carbonado has a light carbon isotopic composition (Vinogradov et al., 1966), fissionogenic noble gas signature (Ozima et al., 1991), non-mantle secondary inclusion mineralogy (Trueb and Buttermann, 1969), and distinctive microstructure (Fettko and Sturges, 1933). These unusual features have caused debates about the origin of carbonado, summarized by McCall (2009). Whatever their origin, their radiogenic ²⁰⁷Pb/²⁰⁶Pb isotopic composition of 0.38 requires them to have formed in the Archean (Ozima and Tatsumoto, 1997; Sano et al., 2002). However, further constraints on which parts of the Archean are model-dependent, and subsequent transport into younger sediments, are poorly understood. Most carbonado studies viewed epigenetic carbonado alteration as a barrier to determining formation. We take the opposite approach, ignoring carbonado genesis and instead using the epigenetic alteration to constrain the history

of carbonado and the erosional and depositional cycles of the São Francisco craton (eastern South America) and Congo sediments in which this diamond is found.

Recent studies (Sautter et al., 2011; Wilson et al., 2012) show that cathodoluminescence (CL) and photoluminescence (PL) features in a few unusual coarse-grained (but still isotopically light) carbonados are related to epigenetic uranium deposition in the cracks and pores, irradiation of the diamond matrix, and subsequent dissolution of the uranium. However, the textural features of the single carbonado grains recently studied (Sautter et al., 2011; Wilson et al., 2012), while similar to each other, are different from the majority of carbonado stones. This work describes a more representative suite of carbonado samples (Table 1), characterizing the uranium precipitation, irradiation, and dissolution features in carbonado of all textural types.

Geology of the Chapada Diamantina and the Diamond Deposits

Carbonado is found in alluvial deposits in Central Africa and the Chapada Diamantina (Diamond Plateau) of Brazil (Derby and Branner,

1905). Stratigraphically, the Chapada Diamantina Group occurs as the upper section of the Espinhaço Supergroup in the Chapada Diamantina region, where the sandstones and conglomerates of the Tombador Formation crop out. These Mesoproterozoic sediments overlie a basement that was metamorphosed during the Transamazonian–Eburnean cycle (2.1–1.9 Ga).

Diamonds in the Chapada Diamantina appear to weather from the Lavras conglomerate of the Tombador Formation, because they are found in streams that drain only this unit, such as the Rio Cachorrinho, south of Lençóis (Sampaio et al., 1994; Pedreira, 1997). The Tombador Formation records a significant source-area change relative to the underlying units by well-documented paleocurrent changes from eastward to westward (Pedreira, 1997). The ages of detrital zircons confirm this (Guadagnin et al., 2015). In addition, the Tombador Formation conglomerates contain green, fuchsite-bearing quartzite clasts, used by garimpeiros (independent prospectors), as an indicator for diamond prospecting; these clasts may have been derived from the pre-Transamazonian Jacobina Basin region (Pedreira, 1997).

The depositional age of the Tombador Formation is 1.436 ± 0.026 Ga, the date of tuffaceous interbeds in its paleo-fluvial plains (Guadagnin et al., 2015). Ozima and Tatsumoto (1997) gave an unsupported radiogenic ²⁰⁷Pb/²⁰⁶Pb of 0.38 for carbonado, which yields a precipitation age of between 3.8 and 2.6 Ga, depending on when the uranium dissolution occurred.

The older limit of this age range predates most of the rocks in the São Francisco craton, which are Paleoproterozoic to Neoproterozoic in age. These diamonds cannot have resided in a crust that had not yet formed, so a geochronologic study of carbonado-bearing streams was performed to determine whether they contained zircons as old as the Pb model age of carbonado. Pedreira (1997) suggested that the green fuchsite extraformational quartzite clasts found in

TABLE 1. SUMMARY OF THE BASIC TEXTURES AND LUMINESCENCE FEATURES OF 21 POLISHED CARBONADOS

Sample	Texture	Color	CL features	Radiation pattern	Source
R-G6	anhedral	orange		bull's-eyes	Brazil
R-F7	microcrystal	orange and green	radiation		Brazil
R-E1	anhedral	orange			Brazil
R-E3	anhedral	orange		bull's-eyes	Brazil
R-E7	microcrystal	multicolored	microstructure		Brazil
R-G1	anhedral	orange and green	radiation	bull's-eyes	Brazil
B-1	microcrystal	multicolored	microstructure		Brazil
B-2	anhedral	orange		bull's-eyes	Brazil
L-3	microcrystal	orange green blue	both	bull's-eyes	Brazil
L-4	anhedral	orange		bull's-eyes	Brazil
L-5	megacrystal	blue growth, multicolored	both	bull's-eyes, crack halos	Brazil
		radiation damage		bull's-eyes	
L-7	anhedral	orange		bull's-eyes	Brazil
L-9	microcrystal	multicolored	microstructure		Brazil
CAR 1	microcrystal	orange, few green grains	both	bull's-eyes	CAR
CAR 2	anhedral	orange		bull's-eyes and flow patterns	CAR
				bull's-eyes	
CAR 11	anhedral	orange			CAR
CAR 16	anhedral	orange and light green	radiation		CAR
CAR 17	anhedral	green, orange highlights	radiation	bull's-eyes	CAR
CAR 21	microcrystal	multicolored	microstructure		CAR
CAR 24	anhedral	orange and green	radiation		CAR
CAR 25	anhedral	green with orange highlights	radiation	bull's-eyes	CAR

Note: CAR—Central African Republic.

the conglomerates are related to quartzite with a green fuchsite matrix in the Jacobina Basin (Teles et al., 2015).

METHODS

Of the 21 carbonados studied, 16 (8 from Central African Republic and 8 from Brazil) were purchased from dealers or donated by other researchers. Study of carbonado sourced from intermediaries was common in the 20th century. Samples procured this way exhibit isotopic, microstructural, and spectroscopic similarities identifying them as a single population. To better understand the sedimentary context, an additional five carbonados were bought from a garimpeiro in Lençóis, Bahia, Brazil, who had panned them from local streams. Rock and heavy mineral separates from these streams were collected using methods described in the GSA Data Repository¹.

Imaging and spectroscopic studies were done on 21 carbonado stones from Central African Republic and Brazil; of these, textural and luminescence defect information from three samples have been published. Grayscale CL images of carbonados B-1 and CAR-2, along with CL and PL spectra from B-1, were presented by Magee and Taylor (1999). Hyperspectral imagery of carbonado L-5 was presented by Wilson et al. (2012). The imaging and spectrographic techniques are detailed in the Data Repository.

¹GSA Data Repository item 2016176, methods, carbonado additional textural and spectral details, pore mineral Chemistry, radiation damage, Raman and photoluminescence, and detrital zircon ages, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

In situ mass spectrometry consisted of the following: the Pb isotopic composition of the florencite minerals in Central African Republic carbonado pores was determined using the SHRIMP II (sensitive high-resolution ion microprobe) at the Research School of Earth Sciences, Australian National University (Canberra), using methods detailed in the Data Repository.

Detrital zircon U-Th-Pb geochronology was performed on zircons from the green extraformational clasts (Pedreira, 1997) of the Lavras conglomerate of the Tombador Formation, on zircons from the Rio Cachorrinho, and on one of the green Jacobina quartzites, which was correlated with the Tombado clasts (Pedreira, 1997). These zircons were reanalyzed using the SHRIMP IIe at Geoscience Australia (Symonston, Australia). Methodological details are provided in the Data Repository.

RESULTS

The carbonados show a number of textural types (see the Data Repository), and the microtextures and luminescence features are summarized in Table 1. Although previous publications have focused on texturally interesting carbonados (Magee and Taylor, 1999; Sautter et al., 2011; Wilson et al., 2012), most of these carbonados have anhedral textures. The coarse-grained texture of carbonado L-5, studied in detail using hyperspectral imagery (Wilson et al., 2012), is unique in this collection. All of the other non-anhedral grains have a microporphyritic texture. All 21 specimens show at least some change in CL response associated with pores. Despite the microtextural variations, some examples of all textural types show bull's-eye halos, and extensive radiation damage along cracks or on outside surfaces (Fig. 1; Figs. DR3–DR7 in the Data

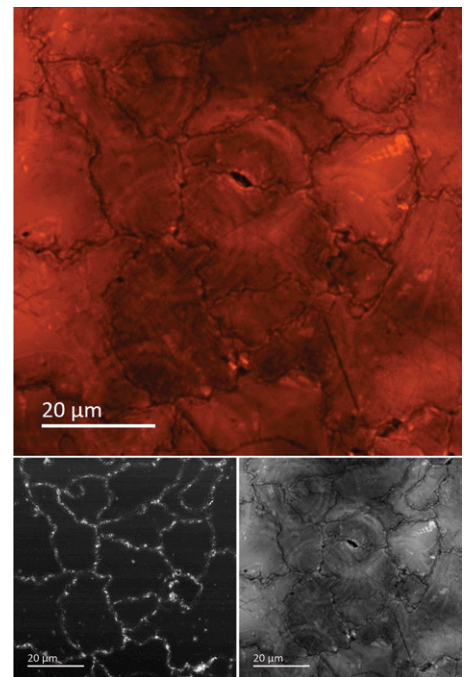


Figure 1. Scanning electron microscopy-based color cathodoluminescence (CL) image of carbonado RG-1 from Brazil, showing radiation damage halos resulting from alpha particles released during uranium series decay. Bottom left panel is an electron image showing grain boundaries; bottom right panel is a panchromatic (visible and ultraviolet) CL image showing concentric circles that represent damage zones resulting from different portions of the U decay chain that emit of alpha particles with differing characteristic energies. Images courtesy of the Smithsonian Institution (Suitland, MD, USA).

Repository). No features are consistent with Th irradiation.

The Pb isotopic composition for the florencite in Central African Republic carbonado is both modern and common (Fig. 2). This is similar to the Pb isotopic compositions of the acid washes from carbonado combustion experiments (Ozima and Tatsumoto, 1997), and yields additional evidence that the pores of carbonado are open to exchange with the environment.

The detrital zircon geochronology data of the sediments from the Rio Cachorrinho, which drains the Lavras conglomerate of the Tombador Formation near Lençóis, show significant zircon populations from the 2.1 Ga Transamazonian–Eburnean cycle, with a smaller Neoproterozoic population and occasional Paleoproterozoic to Mesoproterozoic grains present in the zircon population (Fig. DR11; Table DR3).

The detrital zircon patterns from the extraformational green quartzite clasts and the Jacobina quartzites are strikingly different from the stream sediments, because all of those zircons are Paleoproterozoic, and the Paleoproterozoic and Neoproterozoic grains that dominate the entire stream population are absent (Fig. 3; Tables DR6 and DR7).

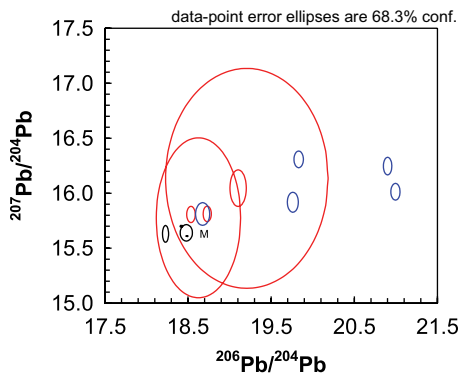


Figure 2. Isotopic composition of florencite Pb (black) compared to the previously reported isotopic composition of Pb leached from carbonado (red), and the Pb isotopic composition of bulk carbonado (blue) (Ozima and Tatsumoto, 1997).

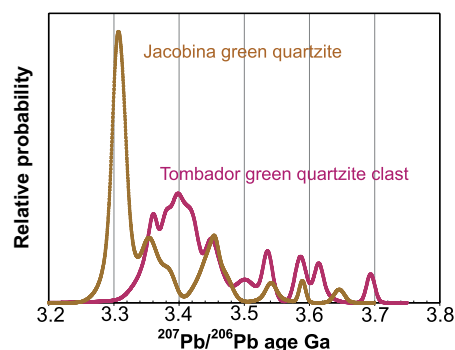


Figure 3. SHRIMP (sensitive high resolution ion microprobe) detrital zircon $^{207}\text{Pb}/^{206}\text{Pb}$ ages for the green clasts from the Lavras conglomerate of the Tombador Formation (Brazil) (purple) and a fuchsitic quartzite from the Jacobina Group (tan).

DISCUSSION

The luminescence and textural data show that the carbonados with anhedral microtextures, although previously reported (Kagi et al., 2007; Yokochi et al., 2008), have been under-represented in more recent defect-related luminescence studies (Rondeau et al., 2008; Sautter et al., 2011; Wilson et al., 2012). All carbonado samples studied here show the same U-related defect luminescence features seen in detailed studies of coarsely crystalline carbonado grains. The radiation patterns are consistent with U precipitation in the pores and cracks of carbonado. The modern common Pb composition of florencite shows that carbonado pores are still open to pore-water exchange with the environment, confirming previous textural observations (Trueb and Butterman, 1969).

The Rio Cachorrinho stream detrital zircon geochronology is similar to published lower Tombador sandstone data (Guadagnin et al., 2015), for which age clusters represent the main tectonic cycles of the Chapada Diamantina basement. The Jacobina quartzite and Tombador

green clast detrital zircon data are similar to each other in that the youngest zircons are Paleoproterozoic, almost 2 b.y. older than the Tombador deposition age. However, the Tombador data lack the large 3.308 ± 0.003 Ga population that dominates the Jacobina data, and the broad 3.420–3.380 Ga Tombador zircon population is smaller in the Jacobina quartzite. The Jacobina data are consistent with recent work from this region (Teles et al., 2015).

Implications for Carbonado Geochronology

The best constraint on the unsupported Pb, He, Kr, and Xe radiogenic isotopes is the $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratio of 0.38 (Ozima et al., 1991; Ozima and Tatsumoto, 1997). Unlike the closed system $^{207}\text{Pb}/^{206}\text{Pb}$ equation, which has a unique answer for a given $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, the equation for a system with U loss consists of paired precipitation times (t_p) and dissolution times (t_d):

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \frac{1}{137.8} \frac{e^{235\lambda_p t_p} - e^{235\lambda_d t_d}}{e^{238\lambda_p t_p} - e^{238\lambda_d t_d}} \quad (1)$$

When $t_d = 0$, this equation simplifies to the closed system $^{207}\text{Pb}/^{206}\text{Pb}$ age equation commonly used in geochronology ($e^0 = 1$). For each t_d between t_p and 0, there is a corresponding residence time ($t_p - t_d$), and a unique pair of t_d and t_p . For a $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.38, varying t_d from 0 to t_p varies t_p from 2.56 and 3.83 Ga. It is important to note that despite some misunderstanding in the literature (Haggerty, 2014), this is not an uncertainty envelope. Rather, it is a range of model outputs, which depend on the time of uranium dissolution (t_d). Figure 4 shows the paired t_p and t_d curves, with various potential geologic triggers on the y-axis. The red line at a radiation duration of 0.2 b.y. (Fig. 4) indicates the minimum time required to accumulate the implanted helium (Ozima et al., 1991), assuming all pore space is filled with uraninite. This represents the shortest physically plausible U residence time.

As seen in Figure 4, the precipitation age required for U dissolution at the 1.436 ± 0.026 Ga time of the Tombador Formation is 3.322 ± 0.013 Ga. This corresponds well with the maximum deposition age of the Tombador green quartzite clasts (Fig. 3). Thus the most parsimonious explanation for the implanted Pb isotopic value is uranium precipitation in the pores and cracks of carbonado at ca. 3.322 Ga, a reasonable deposition age for the source rock of the Tombador green sandstone clasts. The U then dissolves in the next sedimentary cycle at the ca. 1.436 Ga time of Tombador Formation deposition. These calculations do not include any uncertainty component on the 0.38 model $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (Ozima and Tatsumoto, 1997); changing the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio by 0.01 changes the modeled ages by ~ 0.045 b.y.

The isotopic similarity of radiogenic Pb in Central African Republic and Brazilian carbonados (Ozima and Tatsumoto, 1997; Sano et al.,

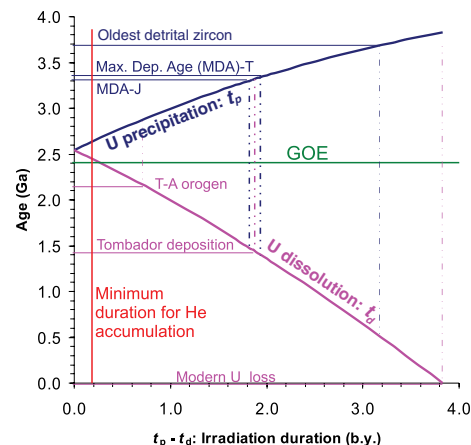


Figure 4. Uranium precipitation and dissolution age curves required to yield the Ozima and Tatsumoto (1997) $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.38 (precipitation time is t_p ; dissolution time is t_d). The minimum accumulation time from unsupported noble gases (Ozima et al., 1991) is shown as a red line. The great oxidation event (GOE) is shown as a green line. Various geological events that could trigger U precipitation or dissolution are shown on the left; tie lines show when the associated dissolution or precipitation must have occurred to yield the observed $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. The oldest detrital zircon and maximum deposition (Max. Dep.) age for the Tombador (T) green quartzite clasts and correlated Jacobina (J) quartzites are from this study. The Transamazonian (T-A) orogen is from the ca. 2.1 Ga sedimentary zircon peak in these sediments. The Tombador deposition age is from Guadagnin et al. (2015). The temporal pairing of the maximum deposition age of the Tombador green quartzite clasts and the deposition age of the Tombador Formation represents the simplest model for when uranium was precipitated in and dissolved from carbonado.

2002) suggests that they shared a common history between t_p and t_d . The erosion event that produced the detritus that formed the Tombador sediments may have also transported carbonado to the Congo portion of the craton. Alternatively, an additional cycle of uplift and erosion prior to the opening of the Atlantic Ocean (such as the Brasiliano orogeny) could have remobilized and transported carbonado from the Mesoproterozoic Brazilian sediments to Africa.

Implications for Archean Oxygen

The Archean atmosphere is traditionally regarded as too reducing to mobilize U through oxidation, and pyrite and Au mineralization in the Jacobina conglomerates on a large scale supports this suggestion (Teles et al., 2015). However, recent studies have indicated the presence of transient whiffs of oxygen in the Archean, particularly in terrestrial settings (Anbar et al., 2007; Crowe et al., 2013; Mukhopadhyay et al., 2014). Furthermore, the benthic hypothesis (Lalonde and Konhauser, 2015), backed up with a modern example (Sumner et

al., 2015), suggests that oxygen produced in the near subsurface could react with multivalent matrix or groundwater elements without ever interacting with the atmosphere. The Pb isotopic constraints for carbonado require it to have gained its uranium in the Archean. Our preferred ca. 3.323 Ga precipitation age is somewhat older than the oldest oxidized paleosol (3.29–3.02 Ga) and 3.22 Ga evidence for pore-dwelling microfossils (Mukhopadhyay et al., 2014; Homann et al., 2016).

Due to the relative scarcity of diamonds in the bulk sedimentary rock, only a tiny proportion of the bulk-rock U needs to be mobilized to account for the U enrichment in these diamonds. Because diamond surfaces (including the grain boundaries of individual diamond crystallites in carbonado) are oleophilic, the carbonado can trap hydrocarbons to reduce dissolved, oxidized U, precipitating the U along carbonado grain boundaries where the radiation damage features show it must have resided.

The oxygen activity required to mobilize U as UO_2^{2+} is lower (Takeno, 2005) than what is required for the Ce oxidation (Mukhopadhyay et al., 2014) or Cr oxidation (Crowe et al., 2013) reported in Mesoarchean paleosols. So, oxygen production in the late Paleoproterozoic need not have been as high as in the Mesoarchean. Uranium mobilization is enhanced by low pH, while Cr mobilization and Ce immobilization are facilitated by high pH, suggesting different or variable aqueous conditions.

Our preferred deposition age is close to the transition time between the large $\Delta^{33}S$ deviations of the Eoarchean and the modest $\Delta^{33}S$ deviations of the Mesoarchean (Farquhar et al., 2010). A study of the sulfur isotope systematics of the Jacobina sediments might yield further insight into the global redox systems operating at that time.

CONCLUSIONS

The Pb systematics of carbonado require precipitation of uranium in carbonado pores and cracks in the Archean. The benthic perspective (Lalonde and Konhäuser, 2015) allows this, and constraints on the timing of Tombador deposition (Guadagnin et al., 2015) imply late Paleoproterozoic U precipitation. Unlike previous studies of paleosols and black shales (Anbar et al., 2007; Crowe et al., 2013; Mukhopadhyay et al., 2014; Stüeken et al., 2015), which identified oxidation via bulk-rock techniques of trace element geochemistry and stable isotopic fractionation, this study comes to the same conclusions using detrital minerals and radiogenic isotopes. While most carbonado research of the past 20 years has focused on determining the origin of carbonado, it may be that studying its epigenetic history reveals evidence for the earliest traces of oxygen in Earth's crust.

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REFERENCES CITED

- Anbar, A.D., et al., 2007, A whiff of oxygen before the Great Oxidation Event? *Science*, v. 317, p. 1903–1906, doi:10.1126/science.1140325.
- Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., and Canfield, D.E., 2013, Atmospheric oxygenation three billion years ago: *Nature*, v. 501, p. 535–538, doi:10.1038/nature12426.
- Derby, O., and Branner, J., 1905, The geology of the diamond and carbonado washings of Bahia, Brazil: *Economic Geology and the Bulletin of the Society of Economic Geologists*, v. 1, p. 134–142, doi:10.2113/gsecongeo.1.2.134.
- Farquhar, J., Wu, N., Canfield, D.E., and Oduro, H., 2010, Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits: *Economic Geology and the Bulletin of the Society of Economic Geologists*, v. 105, p. 509–533, doi:10.2113/gsecongeo.105.3.509.
- Fettke, C.R., and Sturges, F.C., 1933, Structure of carbonado or black diamond: *American Mineralogist*, v. 18, p. 172–174.
- Guadagnin, F., Chemale, F., Jr., Magalhães, A.J.C., Santana, A., Dussin, I., and Takehara, L., 2015, Age constraints on crystal-tuff from the Espinhaço Supergroup—Insight into the Paleoproterozoic to Mesoproterozoic intracratonic basin cycles of the Congo–São Francisco Craton: *Gondwana Research*, v. 27, p. 363–376, doi:10.1016/j.gr.2013.10.009.
- Haggerty, S.E., 2014, Carbonado: Physical and chemical properties, a critical evaluation of proposed origins, and a revised genetic model: *Earth-Science Reviews*, v. 130, p. 49–72, doi:10.1016/j.earscirev.2013.12.008.
- Homann, M., Heubeck, C., Bontognali, T.R.R., Bouvier, A.-S., Baumgartner, L.P., and Airo, A., 2016, Evidence for cavity-dwelling microbial life in 3.22 Ga tidal deposits: *Geology*, v. 44, p. 51–54, doi:10.1130/G37272.1.
- Kagi, H., Sato, S., Akagi, T., and Kanda, H., 2007, Generation history of carbonado inferred from photoluminescence spectra, cathodoluminescence imaging, and carbon-isotopic composition: *American Mineralogist*, v. 92, p. 217–224, doi:10.2138/am.2007.1957.
- Lalonde, S.V., and Konhäuser, K.O., 2015, Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis: *National Academy of Sciences Proceedings*, v. 112, p. 995–1000, doi:10.1073/pnas.1415718112.
- Magee, C.W., and Taylor, W.R., 1999, Constraints from luminescence on the history and origin of carbonado, in Gurney, J.J., et al., eds., *Proceedings of the International Kimberlite Conference 7: Cape Town, South Africa, Red Roof Design*, p. 529–532.
- McCall, G.J.H., 2009, The carbonado diamond conundrum: *Earth-Science Reviews*, v. 93, p. 85–91, doi:10.1016/j.earscirev.2009.01.002.
- Mukhopadhyay, J., Crowley, Q.G., Ghosh, S., Ghosh, G., Chakrabarti, K., Misra, B., Heron, K., and Bose, S., 2014, Oxygenation of the Archean atmosphere: New paleosol constraints from eastern India: *Geology*, v. 42, p. 923–926, doi:10.1130/G36091.1.
- Ozima, M., and Tatsumoto, M., 1997, Radiation-induced diamond crystallization: Origin of carbonados and its implications on meteorite nanodiamonds: *Geochimica et Cosmochimica Acta*, v. 61, p. 369–376, doi:10.1016/S0016-7037(96)00346-8.
- Ozima, M., Zashu, S., Tomura, K., and Matsuhisa, Y., 1991, Constraints from noble-gas contents on the origin of carbonado diamonds: *Nature*, v. 351, p. 472–474, doi:10.1038/351472a0.
- Pedreira, A.J., 1997, Sistemas deposicionais da Chapada Diamantina Centro-oriental, Bahia: *Brazilian Journal of Geology*, v. 27, p. 229–240.
- Rondeau, B., Sautter, V., and Barjon, J., 2008, New columnar texture of carbonado: Cathodoluminescence study: *Diamond and Related Materials*, v. 17, p. 1897–1901, doi:10.1016/j.diamond.2008.04.006.
- Sampaio, D.R., Costa, E.D.A.d., and Neto, M.C.A., 1994, Diamantes e carbonados do alto Rio Paraguaçu: Geologia e potencialidade econômica: *Arquivos Abertos*, p. 1–23.
- Sano, Y., Yokochi, R., Terada, K., Chaves, M.L., and Ozima, M., 2002, Ion microprobe Pb-Pb dating of carbonado, polycrystalline diamond: *Precambrian Research*, v. 113, p. 155–168, doi:10.1016/S0301-9268(01)00208-X.
- Sautter, V., Lorand, J.-P., Cordier, P., Rondeau, B., Le Roux, H., Ferraris, C., and Pont, S., 2011, Petrogenesis of mineral micro-inclusions in an uncommon carbonado: *European Journal of Mineralogy*, v. 23, p. 721–729, doi:10.1127/0935-1221/2011/0023-2154.
- Stüeken, E.E., Buick, R., and Anbar, A.D., 2015, Selenium isotopes support free O_2 in the latest Archean: *Geology*, v. 43, p. 259–262, doi:10.1130/G36218.1.
- Sumner, D.Y., Hawes, I., Mackey, T.J., Jungblut, A.D., and Doran, P.T., 2015, Antarctic microbial mats: A modern analog for Archean lacustrine oxygen oases: *Geology*, v. 43, p. 887–890, doi:10.1130/G36966.1.
- Takeno, N., 2005, Atlas of Eh-pH diagrams: Intercomparison of thermodynamic databases: *Geological Survey of Japan Open File Report 419*, 285 p.
- Teles, G., Chemale, F., Jr., and de Oliveira, C.G., 2015, Paleoproterozoic record of the detrital pyrite-bearing, Jacobina Au-U deposits, Bahia, Brazil: *Precambrian Research*, v. 256, p. 289–313, doi:10.1016/j.precamres.2014.11.004.
- Trueb, L., and Butterman, W.C., 1969, Carbonado: A microstructural study: *American Mineralogist*, v. 54, p. 412–425.
- Vinogradov, A.P., Kropotova, O.I., Orlov, Y.L., and Grinenko, V.A., 1966, Isotopic composition of diamond crystals and carbonado: *Geokhimiya*, v. 12, p. 1395–1397.
- Wilson, N.C., MacRae, C.M., Torpy, A., Davidson, C.J., and Vicenzi, E.P., 2012, Hyperspectral cathodoluminescence examination of defects in a carbonado diamond: *Microscopy and Microanalysis*, v. 18, p. 1303–1312, doi:10.1017/S1431927612013578.
- Yokochi, R., Ohnenstetter, D., and Sano, Y., 2008, Intra-grain variation in $\delta^{13}C$ and nitrogen concentration associated with textural heterogeneities of carbonado: *Canadian Mineralogist*, v. 46, p. 1283–1296, doi:10.3749/canmin.46.5.1283.

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