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LEAVES IN IRON OXIDE: REMARKABLE PRESERVATION OF A NEOGENE FLORA FROM NEW CALEDONIA

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1 ABSTRACT: A Neogene hematite-goethite concretionary 'ironstone' horizon in lateritized 2 fluvial sediments in the Massif du Sud of New Caledonia yields abundant fossil 3 dicotyledonous angiosperm leaves. The leaves are preserved in iron oxide, mainly goethite, 4 which replicates the morphology and anatomy of the leaf tissues and comprises 73% of the 5 matrix. Organic remains are minimal and associated with aluminosilicate clay. Leaf tissues 6 are preserved three-dimensionally in multiple ways including casts/molds, 7 permineralization/petrifaction, and replacement. Although the mesophyll is less well 8 preserved, reflecting its greater susceptibility to decay, cellular details of vascular and 9 epidermal tissues are commonly evident. Analyses of leaves from an analogous modern 10 setting reveal the early encrustation and impregnation of tissues by amorphous iron-oxides 11 and clays in association with a microbial biofilm. We propose a taphonomic model in which 12 the fossil leaves, like their modern counterparts, were permeated by iron oxides due to the 13 high availability of iron derived from weathering of ultramafic basement. In contrast to the 14 iron-rich aluminosilicate coatings that form in relatively iron-poor settings, the unusually 15 high concentration of dissolved iron oxides permitted rapid anatomical preservation.

INTRODUCTION

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18 A role for iron in the preservation of leaf impressions in the fossil record has long been 19 recognized (Krystofovich 1944; Spicer 1977). Such impression fossils provide a window into 20 ancient vegetation in sediments deposited in oxidizing conditions (e.g., upper units of the Clarkia 21 lagerstätte, Idaho, USA: Smiley et al. 1975). However, despite the high fidelity preservation of 22 surface details in some cases (e.g., Dakota Sandstone: Retallack and Dilcher 2012), anatomy 23 rarely survives and these iron-coated leaves provide limited morphological information (Crane 24 and Dilcher 1984). In contrast, permineralized leaves - those in which tissues have been 25 impregnated by minerals and are preserved in three-dimensions - retain more biological 26 information (Schopf 1975; Spicer 1989; Locatelli 2014). The most common minerals involved in 27 this type of preservation are silica (e.g., the Devonian Rhynie Chert), calcium carbonate (e.g., 28 coal balls, travertines), and pyrite (e.g., the Eocene London Clay) (Locatelli 2014). Where iron 29 oxides preserve plant fossils in three dimensions (e.g., Mohr and Friis 2000) this is usually the 30 result of *in situ* weathering of original pyrite. Primary permineralization in iron oxide has been 31 reported from the Permian Clear Fork Group red beds in Texas (Chaney et al. 2009), although 32 most of the leaves are preserved as organic compressions, and from Miocene channel iron 33 deposits in the Pilbara region of Western Australia (Morris and Ramanaidou 2007; Ramanaidou 34 and Morris 2010). More recently a diverse biota from the Miocene McGraths Flat in New South 35 Wales has been described with cellular details preserved in iron oxides (McCurry et al. 2022). 36 Here we describe the taphonomy of an exceptionally preserved fossil flora from New Caledonia 37 which includes angiosperm leaves, seeds and flowers, gymnosperm leaves, with rare associated 38 insects, in Neogene fluvial and lacustrine deposits developed on ultramafic basement (Bourdon

39	and Podwojewski 1988; Locatelli 2013; Garrouste et al. 2021). The leaves preserve cellular
40	detail in three-dimensions in primary iron oxides precipitated externally, at least initially, on a
41	microbially mediated iron-rich clay template. We compare these results to analyses of modern
42	leaves collected in an iron-rich stream in New Caledonia and offer a taphonomic model for this
43	unusual form of fossilization. Microbial biofilms and authigenic mineralization play a role in the
44	preservation of leaves, even in very iron rich settings.
45	
46	GEOLOGICAL SETTING
47	
48	The main island of New Caledonia, the Grande Terre, consists of a Gondwanan basement
49	that separated from the eastern margin of Australia in the Late Cretaceous (Hayes and Ringis
50	1973; Uruski and Wood 1991; Gaina et al. 1998; Eissen et al. 1998; Chevillotte et al. 2006;
51	Maurizot and Vendé-Leclerc 2009; Yang et al. 2013). After the split from Gondwana, the island
52	underwent a complex series of tectonic events, most notably the obduction of an ultramafic
53	ophiolite sequence during the late Eocene (38-34 Ma) now subdivided by tectonics and erosion
54	into several units of which the Massif du Sud, in the south of New Caledonia, is the largest
55	(Pelletier 2006; Maurizot and Collot 2009; Maurizot and Campbell 2020). The tectonic
56	chronology is summarized in a number of publications (Crawford et al. 2003; Sdrolias 2003;
57	Cluzel et al. 2012; Maurizot and Collot 2009; Maurizot and Mortimer 2020).
58	Following obduction, a first episode of extensive lateritization (Herbillon and Nahon 1988)
59	of the ultramafic rocks developed a thick regolith topped by ferricrete. Tropical weathering of
60	the ultramafic ophiolite probably occurred as soon as the early Oligocene and continued after the
61	early Miocene, as evidenced by a series of ferricrete-capped terraces and paleolaterites within

62 early Miocene deposits (Chevillote et al. 2006; Sevin et al. 2011). Early Miocene uplift resulted 63 in regolith erosion, the products of which accumulated in small intermontane basins, which were 64 in turn subject to weathering and the formation of a new ferricrete cap. New Caledonia has been 65 moving northward within the tropical belt since the Miocene (Sdrolias et al. 2003) and terrestrial 66 temperatures have remained relatively constant (within 2°C) for the last 6 million years (Tardy 67 and Roquin 1998). The present geological landscape of the Massif du Sud (Folcher et al. 2015) is 68 a result of erosion. Laterization of the peridotite results in the leaching of Si and Mg downward, 69 concentrating Fe, Ni, and Co in the upper layers of oxisol, the ferricrete cap, and underlying red 70 limonite (Yang et al. 2013): Fe comprises up to 40% by weight of these layers, primarily in the 71 form of goethite (Chevillote et al. 2006). The erosion and transport of the soils and ferricrete cap 72 resulted in the accumulation of goethite-dominated sediments in fluvio-lacustrine deposits, both 73 as transported grains and authigenic minerals (Sevin et al. 2012). Within the fluvio-lacustrine 74 sediments, and later within the soils, concretionary ironstone horizons (duricrusts) formed in situ 75 with the precipitation of hematite and goethite cements around existing grains, filling voids and 76 greatly reducing the porosity and permeability of the horizon (Sevin et al. 2011; Folcher et al. 77 2015). Duricrusts commonly contain root casts and trunks preserved in growth position (Folcher 78 et al. 2015; Sevin et al. 2020).

Neogene (post 25 Ma) fluvio-lacustrine deposits (Guillon et al. 1972; Maurizot and Collot 2009) are distributed across the surface of the southernmost portion of the Grande Terre (Fig. 1). Many of these deposits are concealed beneath the recent regolith, but several have been eroded and provide good exposure (Folcher et al. 2015). The timing of their deposition is unknown, as the iron-oxide dominated sediments are not suitable for radiogenic dating, lack index fossils, and

84	paleomagnetic dating techniques reveal ages ranging from latest Oligocene to Holocene (Sevin et
85	al. 2012; Folcher et al. 2015; Maurizot et al. 2020; Sevin et al. 2020).
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87	MATERIALS AND METHODS
88	
89	Fossil Leaves
90	Samples of fossil dicotyledonous angiosperm leaves (Fig. 2) were collected from a \sim 2 cm
91	thick duricrust of ferruginous silt and claystone within uplifted fluvio-lacustrine deposits in the
92	Rivière des Lacs Basin (Garrouste et al. 2021, Supplementary Figure 7) toward the southern end
93	of the Massif du Sud (Fig. 1). The roadside exposure is along the Route de Carénage,
94	approximately 200 m north of the entrance to the Chutes de la Madeleine Natural Reserve (-
95	22.229°, 166.851°) (Fig. 1). Abundant dicotyledonous angiosperm leaves dominate the flora,
96	which also includes flowers, seeds, and wood (Garrouste et al. 2021). The samples are the
97	property of the government of New Caledonia, Service Géologique de la Nouvelle-Calédonie
98	(SGNC) and are held by the Direction de l'Industrie, des mines et de l'énergie de la Nouvelle-
99	Calédonie (DIMENC).
100	
101	Modern Leaves
102	Leaves from a small stream south of Les Chutes de Madeleine (-22.273°, 166.931°) were
103	collected for investigation as a modern analog because conditions in this stream are likely similar
104	to those in the fluvial system in which the fossils were deposited. The vegetation surrounding the
105	stream is composed primarily of shrubs adapted to the acidic nature of the iron-rich, clay-poor
106	oxisols that occur in the study area (Jaffré 1992; Isnard et al. 2016).

107 The stream was at low, dry-season levels at the time of collection (April 2013), as indicated 108 by terraces on the stream banks and the accumulation of leaves and other debris higher on the 109 bank. Fifteen leaves were collected from the bottom of a shallow pool in the stream, and fifteen 110 from within the top layer of sediment on the stream bank; total sediment thickness was not 111 measured. The ages of the two sample sets are unknown, and they may represent multiple 112 wet/dry seasons. The leaves were dried slowly by placing them in absorbent paper in a 113 temperature-controlled room to retain their integrity and prevent any significant further decay. 114 115 Microscopy and EDS and XRD Analysis 116 A total of 40 dicotyledonous angiosperm leaf fossils were examined using light microscopy

(Fig. 2). Morphological and anatomical preservation of both the fossil and modern leaves were
investigated using scanning electron microscopy (SEM) (Figs 3, 5–8) and elemental composition

119 was analyzed using electron-dispersive-X-ray spectroscopy (EDS) (Figs 3, 8).

120 Material for SEM was obtained from the margins of fossil leaves by extracting small portions 121 of leaf and matrix with a scalpel; 25 such fragments were sampled. Three polished thin sections 122 were made for elemental and mineralogical analysis. Six modern leaves, three from the stream 123 bed and three from the bank sediment, were sampled for SEM analysis. Samples were mounted 124 on aluminum stubs, platinum coated using a Cressington 108 Auto Sputter Coater and examined 125 using a FEI XL-30 field emission gun environmental SEM equipped with an EDAX energy 126 dispersive X-ray spectrometer. Point spectra were taken from different tissues at an accelerating 127 voltage of 10 kV and collection time of 100 seconds.

Material for X-ray diffraction analysis was scraped from the surface of modern leaves with a scalpel. The powder sample was analyzed with a bench-top MiniFlex 600 (Rigaku) which uses

130 Cu radiation and a wide area scintillation counter detection system. It was operated at 600W 131 (40kV - 15mA) to collect data in reflection mode with a 2 θ scan range of 3° to 90° at 5°/minute 132 and a step size of 0.02°. The data were analyzed using Rigaku Data Analysis Software (PDXL 133 2).

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Raman Spectroscopy

136 Four standard 30 µm thick petrographic thin sections were cut and polished to create vertical 137 sections through the fossil leaf-bearing concretionary layer and transverse sections through the 138 leaves themselves. Raman spectra were obtained using a Horiba Jobin Yvon Labram HR800 139 spectrometer equipped with a 532 nm laser with a hole size of 300 μ m, a slit size of 100 μ m, and 140 a grating of 1800 grooves/mm. Spectra were acquired for 6 seconds with 10 repetitions. A 141 neutral density filter was used to reduce the laser power as iron oxides other than hematite are 142 prone to burning, which results in shifting and transformation of the spectrum (Hanesch 2009). A 143 total of 30 grains, 5 each from 3 different fossil leaves and 5 each from the matrix associated 144 with the 3 different leaves, were analyzed for each thin section. At low magnification, the darker 145 red matrix and orange to yellow leaves are markedly distinct. Leaf and matrix areas were 146 identified, and grains within those regions were selected at random, providing they were large 147 enough to sample (> 2 μ m diameter).

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RESULTS

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Fossil Leaves

152	Composition .—EDS maps and point spectra on the thin sections show that the fossil leaves
153	are composed predominantly of a mixture of iron oxides and aluminosilicate clays (Fig. 3).
154	Residual carbonaceous material, revealed by backscatter electron imaging as dark areas within
155	the leaf and by elemental mapping (Fig. 3B, 3C), is restricted to discrete particles encased in a
156	very fine-grained iron-rich clay (Fig. 3B, 3C). The rest of the leaf tissue is composed of iron
157	oxide, with small amounts of carbon, aluminum and silicon (Fig. 3C, Supplement). The matrix is
158	composed of carbon-, aluminum- and silicon-poor iron oxides, which are enriched in chromium
159	(Fig. 3C, supplement).
160	Raman spectroscopy identified 4 of the 15 matrix grains (27%) as hematite (Fe ₂ O ₃),
161	evidenced by diagnostic peaks at 225, 300, and 1321 cm ⁻¹ and a weaker peak at 412 (Hanesch
162	2009) (Fig. 4A). The majority of the grains (11, i.e., 73%) were goethite (α -FeOOH), evidenced
163	by diagnostic peaks at 385 and weaker ones at 225, 299, 548, and 681 cm ⁻¹ (Hanesch 2009) (Fig.
164	4B). The predominantly fine-grained isodimensional crystalline nature of the matrix with
165	acicular outgrowths is also consistent with a mixture of hematite and goethite (Schwertmann and
166	Latham 1986; Cornell et al. 1989) (Fig. 5A).
167	All 15 grains sampled from the fossil leaves were identified as goethite (Fig. 4C). Figure 4C
168	shows a spectrum characteristic of 12 of the 15 leaf grains sampled; the other 3 leaf grains lacked
169	the definitive peak at 385 cm ⁻¹ but yielded a wide peak at 400 cm ⁻¹ (not figured). This is
170	consistent with other natural samples of goethite ('yellow ochre') and reflects merging of the 385
171	cm ⁻¹ peak with a small one at 417 cm ⁻¹ (Hanesch 2009), a slight shift attributed to different
172	crystallinities of the mineral which was confirmed by SEM analysis. SEM of the leaf tissues
173	revealed mineral forms ranging from acicular crystals and crystal bundles to a nanogranular and
174	amorphous texture. Acicular crystals and crystal bundles range in length from 100 nm to 2 μ m,

175 consistent with the acicular form of goethite crystals that precipitate in void spaces in a silica and 176 aluminum-poor medium (Fig. 5B, 5C) (Fordham et al. 1984; Cornell 1985; Cornell et al. 1987; 177 Schwertmann 1988). The well-defined goethite crystals are found in voids, such as cell lumina, 178 whereas minerals that appear nanogranular to amorphous form a mesh-like fabric comprised of 179 individual crystals on the order of a few tens of nm in length and width (Fig. 5D), which we 180 interpret as very fine-grained iron-rich aluminosilicate clays and iron oxides that were too small 181 to analyze individually using Raman spectroscopy, but for which EDS revealed a composition of 182 predominantly iron, aluminum, silicon, and oxygen. It is this nanogranular to amorphous 183 material that is involved in the fine preservation of both internal (e.g., epidermal cells, veins, 184 stomata) and external (e.g., leaf gland) anatomy.

Anatomical and Morphological Preservation.—SEM of fossil leaf tissues revealed that they are preserved in multiple ways including permineralization/petrifaction (a gradation from retention of organic cell walls to loss and replacement of all carbonaceous remains of the cuticle), replacement, and as casts or molds in iron oxides; individual leaves often exhibit several modes of preservation. The three-dimensionality of the preservation was confirmed by SEM including backscatter electron microscopy (Fig. 6A, 6B).

191 Vascular tissues are usually preserved as hollow tubes with the walls preserved either as a 192 cast or via replacement (Fig. 6C), or as solid bundles, which are likely internal casts (Fig. 6D). 193 Where vascular tissues are preserved as hollow tubes mineral grain size varies, which may 194 indicate precipitation at different rates and times, and boundaries between cells are rarely 195 discernable. Internal casts may preserve individual cells of the vessel lumen (Fig. 6D). In several 196 samples, vascular tissues exhibit evidence of decay followed by replacement: in these cases, the

cellulose-dominated cell wall has decayed leaving lignified secondary cell wall thickenings thatwere subsequently replaced by iron oxides (Fig. 6E).

Mesophyll is the least well preserved of the leaf tissues. Only poor cellular preservation was observed in the thin sections (Fig. 6A), although the overarching structure of some leaves is discernible. Visibility of preserved tissues under the SEM depends on fortuitous fractures in the fossil material: the matrix is cemented so thoroughly that it cannot be removed using needles or other tools. Typically, the mesophyll of leaves has decayed away leaving spaces infilled by iron oxides with no orientation or pattern (Fig. 6J).

205 Epidermal details, including cells, stomata, and glands, are preserved predominantly as 206 molds and casts and via replacement. Stomata were most commonly evident from the interior of 207 the leaf (Fig. 6F). The guard cells of the stomata are preserved as external molds, and the walls 208 of cells surrounding the stomata have been replaced (Fig. 6G). Some epidermal cell walls are 209 preserved as residual cuticle, whereas others have been replaced by iron oxides (Fig. 6H). When 210 cells are preserved as internal casts, coarser mineral grains on the order of several microns mask 211 finer details (Fig. 6I). The walls of epidermal cells can also be replaced by iron oxides, revealed 212 when fractures through the leaf tissue are parallel with the leaf surface (Fig. 6F). Where external 213 epidermal features are preserved via replacement by iron oxides at a cellular level, the 214 distribution and morphology of glands across the leaf surface are evident (Fig. 6K, 6L). No 215 trichomes or trichome bases were observed. 216 There was evidence of microbial biofilms (Pacton et al. 2007) on the surface of some leaves, 217 including a diatom (Fig. 7A) and strands and veils of mineralized extracellular polymeric

218 substances (EPS) (Fig. 7B–D).

219

Modern Leaves

221 Modern leaves collected from stream and bank sediments showed no differences in extent of 222 decay or early diagenesis. Leaves from both settings exhibited a spectrum of decay, damage, and 223 mineralization, from entirely whole with a crust of iron oxides, to partially skeletonized, to 224 almost entirely skeletonized (Fig. 8A). All leaves were covered in a fine layer of iron oxide, up 225 to 0.5 mm thick on some. EDS spectra of the mineral coating revealed an iron-oxide (Fig. 8B), 226 but those closest to the leaf surface contained significantly more aluminum and silicon than the 227 exterior portion of the coating, indicating the presence of aluminosilicate clays in addition to iron 228 oxides (Fig. 8C). The leaves retained significant organic material, but EDS analysis (Fig. 8B) 229 showed that all portions of the leaf were encrusted or impregnated with iron oxides. XRD data 230 showed this material to be predominantly goethite. 231 A transverse section through a leaf sampled for SEM revealed extensive impregnation of the 232 leaf by iron oxides with highest concentrations on the more porous abaxial side (Fig. 8D, 9). The 233 surface of all of the leaves was covered in a poorly crystalline crust and diatom biofilm (Fig. 8A 234 and 8E). The iron oxide crust was similar in thickness across the leaf, although it was 235 discontinuous in places (Fig. 8F). This discontinuity may be an effect of drying and transport 236 after collection. The crust appeared to have precipitated between layers of EPS (Fig. 8E). The 237 appearance of the crust and composition of the leaves (Supplementary figure) is consistent with 238 ferrihydrite (Loeppert and Clarke 1984), a hydrated ferric oxyhydroxide, which previous 239 taphonomic experiments have shown to form on decaying leaves (Dunn et al. 1997). A portion of 240 skeletonized leaf revealed the infilling of void spaces, impregnation of veins, and coating of cell 241 surfaces by iron oxides (Fig. 8G). Two diatom species were found on all leaves sampled (Fig. 242 8H, 8I).

243	
244	DISCUSSION
245	Mode of Preservation
246	Fossil leaves and other plant organs with a coating of iron rich-clays have been reported
247	from strata ranging from Silurian to Recent in age, and the process involved has been
248	investigated via taphonomic experiments and the analysis of fossils (Locatelli 2014).
249	Experiments have shown that the microbial biofilms that form during decay attract metal ions,
250	particularly iron and aluminum (Konhauser and Urrutia 1999). Within days to weeks, iron-rich
251	aluminosilicate clays nucleate and precipitate within the EPS matrix (Konhauser et al. 1998;
252	Locatelli et al. 2017). Clay coatings increase the preservation potential of leaves as they slow
253	the rate of microbial decay and increase the integrity of the leaf over longer timescales,
254	allowing further mineralization or lithification (Dunn et al. 1997; Locatelli 2014). The
255	precipitation of a clay and metal oxide coating normally results only in the preservation of the
256	external leaf surfaces in impressions or the protection of organic tissues within compressions
257	rather than the precipitation of minerals within the leaf as in the New Caledonian fossils.
258	Plant fossil assemblages in which internal tissues are preserved in iron oxides may be the
259	result of in situ weathering of original pyrite, as in the Cretaceous Crato flora from Brazil
260	(Mohr and Friis 2000; Martill et al. 2007). The Permian Clear Fork Group flora from Texas
261	(Mamay 1989; Chaney and DiMichele 2007; Chaney et al. 2009) is a product of direct
262	precipitation of iron oxides. The preservation of the New Caledonian plant fossils appears
263	directly attributable to the unusually high amount of available iron oxides and the rapid
264	formation of duricrust in the weathering profile of the ultramafic basement. In this respect the
265	depositional setting in New Caledonia, both now and in the past, is unusual. The lateritization

266 of ultramafic rocks results in oxisols with a layered profile, the upper layers of which are 267 dominated by iron oxides but are very poor in silicon and aluminum (0.5-1.7%) (Schwertmann 268 and Latham 1986, Fandeur et al. 2009). Analyses of the red limonite sediments (the layer in 269 which ironstone horizons form) on the Koniambo Massif in northern New Caledonia, for 270 example, revealed a composition of 40–75% iron by weight (Yang et al. 2013). Hematite and 271 goethite are the most common minerals in the red limonite and form *in situ* from the 272 weathering products of the underlying peridotite (Sevin et al. 2012). Goethite is the only iron 273 oxide found in oxisols of higher altitude regions (Schwertmann and Latham 1986). In low 274 altitude regions, such as the area of our study, hematite contributes up to 40% of the modern 275 sediments (Schwertmann and Latham 1986), consistent with the results of the Raman analyses 276 of the matrix in which our fossils are preserved. Similar processes preserve plants and insects 277 where schwertmannite and goethite precipitate on their surfaces in the acid drainage from iron 278 sulfide ores in the Rio Tinto system north of Huelva in south-west Spain (Sánchez España et 279 al. 2007; Fernández-Remolar and Knoll 2008). Here, as in New Caledonia, the precipitates 280 forming in the river today are the same as those in the river terrace which, in Spain, are up to 2 281 million years old. The spectacular fossils at McGraths Flat in New South Wales are likewise 282 preserved in goethite with local basalts as the source of iron (McCurry et al. 2022). Travertines 283 may also include bands of goethite, ferrihydrite and other oxides (Arana et al. 1979) and in 284 some cases these preserve plants and insects (Nel and Blot 1990; Kanellopoulos et al. 2019). 285

286

Ferrihydrite, Goethite, and Hematite

Hydrated iron oxyhydroxide ferrihydrite, which is the first iron oxide adsorbed onto
leaves during decay (Dunn et al. 1997), is unstable and quickly undergoes transformation,

289	usually to hematite or goethite, which are the most thermodynamically stable species under
290	oxic conditions, such as those that prevail in the oxisols of New Caledonia (Cornell 1985;
291	Cornell and Giovanoli 1985; Cornell et al. 1987; Cornell and Schwertmann 2006; Fandeur et
292	al. 2009). The transformation of ferrihydrite to either goethite or hematite is controlled by
293	numerous factors, including the amount and type of free sugars, aluminum replacement of
294	iron (III), and water availability (Cornell and Schwertmann 2006 and references therein).
295	Generally, the conditions that favor the transformation of ferrihydrite to goethite (pH 2–5, 9–
296	12; <30°C) greatly inhibit the transformation to hematite and <i>vice versa</i> (Schwertmann et al.
297	2004; Cornell and Schwertmann 2006). Aluminum-replacement of iron in the ferrihydrite
298	matrix can prevent its transformation to goethite (Fritsch et al. 2002).
299	Surface waters and soils from the region where the fossils occur (lowlands; mean annual
300	temperature 23–24°C) are generally acidic with a pH of 4.4–5 (Enright et al. 2001; Read et al.
301	2006). Surface temperatures and pH values within this range favor the transformation of
302	ferrihydrite into goethite on multi-year to decadal timescales (Schwertmann et al. 2004;
303	Cudennec and Lecerf 2006). The preservation of leaves in goethite and its dominance in the
304	surrounding matrix indicate that the pH range was relatively constant. The proportion of
305	matrix consisting of hematite (27%) may reflect a transported fraction or dehydration of the
306	matrix ferrihydrite following fossilization (Schwertmann et al. 2004). Thus the near-total
307	replacement of tissues in the New Caledonian fossil flora by iron oxides suggests preservation
308	within a time window of several years to a few decades. However, the rate of decay and
309	mineral precipitation may have varied during alternating water-logged and well-drained or
310	drying conditions (Spicer 1991; Locatelli 2014). During arid phases the reduction or absence
311	of abundant pore waters may have reduced both the rate of decay and mineral precipitation.

The modern leaves collected from the stream displayed a range of decay states, but the length of time any individual leaf was in the stream is unknown. There was no evidence of crystalline hematite or goethite on these leaves: the amorphous or nano-granular texture of the mineral crust indicates recent authigenic precipitation. The leaves collected from sediments in the stream bank were also encrusted in a similar aluminum-enriched iron oxide.

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CONCLUSION

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Accumulation of the erosion products of laterite profiles developed on ultramafic rocks in 320 321 the Rivière des Lacs Basin in the southern Massif du Sud of New Caledonia has resulted in 322 surface sediments depleted in aluminum and silicon but greatly enriched in highly mobile iron 323 (III) (Read et al. 2006). As observed in the modern fluvial analogue, accumulation of leaves in 324 low-energy pools within a stream resulted in enhanced fossilization potential. Analyses of 325 fossil leaves and modern analogues suggest that microbes, including diatoms and most likely 326 bacteria, colonized the leaf surface as well as other exposed leaf tissues. Associated 327 extracellular polymeric substances (EPS) resulted in biofilms (Fig. 7) on to which dissolved 328 iron, aluminum, and silicon were adsorbed, resulting in the initial microbially-mediated 329 precipitation of iron- and aluminum oxides and aluminosilicate clay minerals (Konhauser 330 1998) (Figs 7, 8). Elemental analyses reveal that these precipitates on both fossil and modern 331 specimens are iron-rich and silicon-poor (Figs 3, 8, Supplement), consistent with the 332 composition of New Caledonian soils and water associated with weathered ultramafic rocks 333 (Enright et al. 2001). The precipitated iron- and aluminum oxides and aluminosilicate clay 334 minerals formed a fine-grained crust on both internal and external surfaces (Figs 6-8,

Supplement), which helped prevent complete collapse of the leaf during burial. The aluminum
content prevents the early-formed amorphous oxides from forming larger crystals (Schulze
and Schwertmann 1984), promoting the preservation of fine morphological details such as
stomata (Fig. 6F, 6G).

339 Aluminum and silicon are depleted by initial microbially-mediated precipitation, and the 340 abundance of iron results in the further precipitation of predominantly iron oxide minerals 341 rather than aluminosilicate clays (Locatelli et al. 2017). Acidic conditions enhanced by decay 342 within the leaf promote the formation of goethite rather than hematite, as evidenced by Raman 343 spectroscopy of leaf tissues (Fig. 4C). The duricrust, in contrast, contains a combination of 344 goethite and hematite, indicating that the sediment pore waters were less acidic (Fig. 4A, 4B), 345 consistent with soil pH measurements from previous studies (Read et al. 2006, table 3). 346 The three-dimensional nature of the fossil leaves (Figs 3A, 6A) and associated, seeds, 347 flowers, and wood fragments indicates that the duricrust formed rapidly, prior to significant 348 decay and collapse. Leaf fossils were not found in the sediments outside the duricrust, 349 indicating that its formation was integral to their preservation. Duricrusts form rapidly when 350 previously waterlogged conditions are followed by dry intervals (Fritsch et al. 2002). The 351 precipitation of dense iron oxide cements reduces the porosity and permeability, which reduces 352 the rate of oxidative destruction of leaf tissues and permits permineralization/petrifaction and 353 replication to occur. Portions of the leaf encased in early aluminosilicate clays and oxides 354 survive as small carbonaceous lenses, but the preservation of anatomy relies very largely on 355 mineralization of morphological features (Fig. 3).

The highly oxidizing fluvial and lateritic environments in New Caledonia are not generally conducive to plant preservation. However, duricrusts with root traces are common features of

358	the New Caledonian fluvio-lacustrine deposits, and although leaf fossils are rare (Folcher et al.
359	2015), those reported here show the potential of duricrust horizons that formed on ultramafic
360	terrains as a source of exceptionally preserved plant fossils.
361	
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FIGURE 1.—Location of the study area in 'Massif du Sud' of New Caledonia with insets
showing position of A) New Caledonia in relation to Australia and B) position of 'Massif du
Sud' within New Caledonia. (Modified from Maurizot and Vende-Leclerc 2009 and Folcher et
al. 2015).

568

FIGURE 2.—Selected angiosperm leaf fossils from Neogene fluvio-lacustrine deposits, 'Massif
du Sud', New Caledonia. A-E) Preservation of venation. A) F-DIM 0170A; B) F-DIM 0171A,

cf. Myrtaceae, sp. 1; C) F-DIM 0172A, Ericaceae; D) F-DIM 0173A; E) F-DIM 0172B, cf.

572 Myrtaceae, sp. 2. F) with G) a detail showing three dimensional and variable preservation of leaf

tissues: F-DIM 0170B. H) Three-dimensional preservation and a cast of leaf tissues: F-DIM
0172C.

575

FIGURE 3.— Backscatter scanning electron micrographs and elemental maps of a section through part of a fossil angiosperm leaf from F-DIM 0170. A) Backscatter electron micrograph of a thin section through part of a fossil leaf (the dark area is an epoxy-filled void). Outline indicates the location of the image in B. B) Backscatter electron micrograph of the edge of the leaf upper surface showing poorly preserved cell outlines and residual dark carbonaceous material scattered in a mineral matrix. C) Elemental maps of the area in B.

FIGURE 4.—Raman spectroscopic analyses of fossil leaves. A) Spectrum characteristic of four
analysed matrix grains, consistent with hematite. B) Spectrum characteristic of the other 11

matrix grains, consistent with goethite. C) Spectrum characteristic of all grains from analysed
fossil leaves, also consistent with goethite.

588

FIGURE 5.—Scanning electron micrographs of mineral textures from F-DIM 0172. **A**) Finegrained texture characteristic of the matrix. **B**) Coarse goethite bundles characteristic of infill preservation within vascular tissues. Inset shows location within a leaf vein (Fig. 6D). **C**) Finegrained goethite bundles characteristic of infill preservation of some vascular tissues and other tissue types. Inset shows location within the vascular tissue. **D**) Nanocrystalline to amorphous texture of mold preservation of stomata and epidermal cells. Inset shows location on a stoma guard cell (Fig. 6G).

596

597 FIGURE 6.—Scanning electron micrographs of fossil angiosperm leaves (A in backscatter 598 mode from F-DIM 0170 (see Fig. 3). B, D, F, G, I, J from F-DIM 0172; E from F-DIM 0170; H, 599 K, L from F-DIM 0173). A) Cross section through part of a three dimensionally preserved leaf 600 showing the difference in intensity between the matrix and fossil resulting from the different iron 601 oxide minerals and trace elements they contain. The black areas are voids. M = mesophyll, Ab =602 abaxial (lower) surface, Ad = adaxial (upper) surface, V = Midrib vein. B) Part of a fossil leaf 603 showing three-dimensional preservation of tissues. M = mesophyll, V = vascular tissues, E = mesophyll604 epidermis. C) Vascular tissue replaced by iron oxides, resulting in hollow tubes. D) Vascular 605 tissue preserved as internal molds. Center of the image lacks clarity of individual cells, while 606 cells on the left of the image are preserved such that individual cells are distinct. E) High fidelity 607 replacement of vascular tissues showing loss of cellulosic cell walls and replacement of lignified 608 secondary cell walls by iron oxides. F) Fracture through a leaf showing the walls of epidermal

cells and stomata replaced with iron oxides. G) Details of a single stoma showing replacement of
cells walls. H) Adaxial epidermis viewed from the inside of a leaf. In some areas, residual cuticle
may be preserved (lower arrow). In others, the cuticle is replaced by iron oxides (upper arrow).
I) Internal mold of epidermal cells infilled with acicular iron oxides. J) Poorly preserved remains
of mesophyll (center) surrounded by internal molds of vascular tissues. K) Leaf gland showing
replacement by iron oxides. L) Leaf fragment showing multiple glands (top) and vascular tissues
preserved as internal molds.

616

FIGURE 7.—Scanning electron microscope images of fossil angiosperm leaves showing
evidence of biofilms (indicated by arrows) from F-DIM 0173. A) Diatom. B) Thin strands of
EPS. C) EPS veils. D) Biofilm strands.

620

621 FIGURE 8.—Modern angiosperm leaves from a stream south of Les Chutes de Madeleine. A) 622 Leaves showing differences in completeness, decay, and encrustation. Left to right: Homalium 623 kanaliense (Salicaceae), Grevillea gillivrayi (Proteaceae), Tristaniopsis glauca (Myrtaceae). B) 624 EDS spectrum of thick mineral crust (point 1 in E) showing an aluminum-bearing iron oxide. C) 625 EDS spectrum of minerals in contact with the leaf (point 2 in H), showing an iron-rich 626 aluminosilicate and iron oxide. D-I) Scanning electron micrographs. D) Transverse section of a 627 leaf impregnated by iron oxides; note the coherent leaf cuticle. E) Biofilm comprised of diatoms 628 (D), their extracellular polymeric substance (E), and mineral crust (1). F) Detail of mineral crust 629 on the abaxial leaf surface; note the coherent leaf cuticle and stomata. G) Partially skeletonized 630 leaf showing the resistance of exposed veins preserved iron oxides. H, I) Two of the different 631 diatoms found on all the leaves examined.

633

634 section of the leaf illustrated in Figure 8D rotated to horizontal, adaxial surface at the top. 635 636 Supplementary figure.—Backscatter scanning electron micrograph and elemental spectra of 637 points within a section through part of the fossil angiosperm leaf from F-DIM 0170 illustrated in 638 Fig. 3. A) Backscatter electron micrograph of a thin section through part of the fossil leaf (the 639 dark area is an epoxy-filled void). Outline indicates the location of the image in B. B) 640 Backscatter electron micrograph of the edge of the leaf upper surface showing poorly preserved 641 cell outlines and residual dark carbonaceous material scattered in a mineral matrix. Numbers 642 correspond to the location of EDS spectra in C. C1) Iron oxide dominated matrix surrounding the 643 leaf. C2) Residual carbonaceous material. C3) Mixed aluminosilicate, iron oxide associated with 644 residual carbonaceous material. C4) Mixed aluminosilicate, iron oxide within the leaf not 645 directly associated with residual carbonaceous material. 646

FIGURE 9.— Backscatter scanning electron micrographs and elemental maps of the transverse



















Supplementary Figure

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