Iron terraces in acid mine drainage systems: A discussion about the organic and inorganic factors involved in their formation through observations from the Tintillo acidic river (Riotinto mine, Huelva, Spain)

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ABSTRACT

Iron terraces that form in acidic mine drainage settings are unique and extreme geomicrobiological systems that can provide highly relevant information about the interaction between microbes and their surrounding aqueous environments. These singular systems can represent, additionally, potential models for the study of ancient geological formations (e.g., banded iron formations, stromatolites) and/or for the cycling of iron on Mars. This work describes geochemical, mineralogical, morphological, and microbiological evidence obtained in the highly acidic and Fe-rich Tintillo River (Riotinto mines, Huelva, SW Spain), which can be used to speculate about the origin and nature of the terraced iron formations (TIFs) that are being currently formed in acid mine drainage environments. The size (up to 36 m long and 1 m thick) and continuity (strong development over 3.5 km) of the iron terraces offer a unique opportunity to study the different organic (mainly microbial) and inorganic processes involved in the construction of these characteristic, travertine-like, sedimentary structures. Evidence presented in this study suggests that both types of processes appear to be controlling factors in the formation and internal arrangement of the TIFs, although no definitive evidence has been found to support the prevalence of any of these mechanisms with respect to another. The photosynthetic production of dissolved oxygen by eukaryotic microorganisms (green algae, euglenophytes, and diatoms) and the Fe-oxidizing metabolism of acidophilic prokaryotes are critical factors for the formation of TIFs, whereas abiotic parameters, such as water composition, flow rate and velocity, or stream channel geometry, also appear to be essential variables.

Keywords: acid mine waters, acidophilic microbes, iron, terraced formations, Tintillo River, Riotinto.

INTRODUCTION AND SCOPES

The presence of ferruginous terraces of millimetric to metric scale is probably the most striking feature observed in acid mine drainage settings worldwide. These terraced iron formations (TIFs) are usually developed during the oxidation and hydrolysis/precipitation of dissolved iron in the acidic solutions after they emerge from waste piles, tailings, or mine portals, and they display a morphological pattern similar to that observed in calcareous travertines formed in Ca^{2+}-HCO_3^-–rich spring waters. TIFs differ from calcareous travertines, however, in their mineralogical composition, which is characterized by hydrous iron (oxy)hydroxides and/or hydroxysulfates (Sánchez-España et al., 2005a, 2005b, 2005c), in agreement with the typical Fe(II)/Fe(III)-SO_4^{2-} chemical composition of most acid mine drainage solutions (Nordstrom and Alpers, 1999).

TIFs have been, until now, the subject of little scientific attention. The most remarkable studies available in the literature have been focused on the acid mine drainage systems of the Carnoulés Pb-Zn mine, France (Leblanc et al., 1996; Casiot et al., 2004) and the Green Valley coal mine, Indiana, USA (Brake et al., 2001, 2002, 2004; Hasiotis et al., 2001). From this research, it is apparent that microbes (including acidophilic bacteria and eukaryotic microorganisms) play a critical role in the construction and internal structure of such iron terraces, via extracellular and intracellular assimilation of iron and other metals. Further, TIFs have been proposed as modern analogs for ancient (Precambrian) banded iron formations (BIF) of the geological record (Hasiotis et al., 2001; Brake et al., 2002), as well as for the Proterozoic and present-day stromatolite-building colonies of cyanobacteria (Leblanc et al., 1996; Brake et al., 2002, 2004), and they have also been considered by other authors as terrestrial equivalents of the iron oxide deposits recently discovered on Mars (Fernández-Remolar et al., 2004). However, the relative importance of the microbial activity with respect to inorganic processes, such as water composition, Fe(III) precipitation rate, stream flow velocity, or channel geometry, has not yet been evaluated. A further and critical question arises about whether the formation of these ocherous terraces is determined by parameters such as stream channel geometry or flow velocity, or if, on the other hand, they control the evolution of such parameters.

The Tintillo River (Huelva, SW Spain) is probably a world-class example of an acid mine drainage–impacted stream in the sense that it is almost entirely formed by highly acidic and metal-rich acid mine drainage solutions emanating from waste piles located near the Corta Atalaya open pit (Riotinto Mines; Fig. 1). This stream course shows chemical, physical, and microbiological features that seem to favor the development of these travertine-like, ferruginous deposits (Sánchez-España et al., 2005a, 2005c). For example, it has:

(1) initially near-anoxic water with a high concentration of dissolved ferrous iron (on the order of 2 g/L Fe[II]) at the source point;

(2) an initially turbulent flow near the source point (downslope of the waste pile) with successive, centimeter-scale water falls that promote

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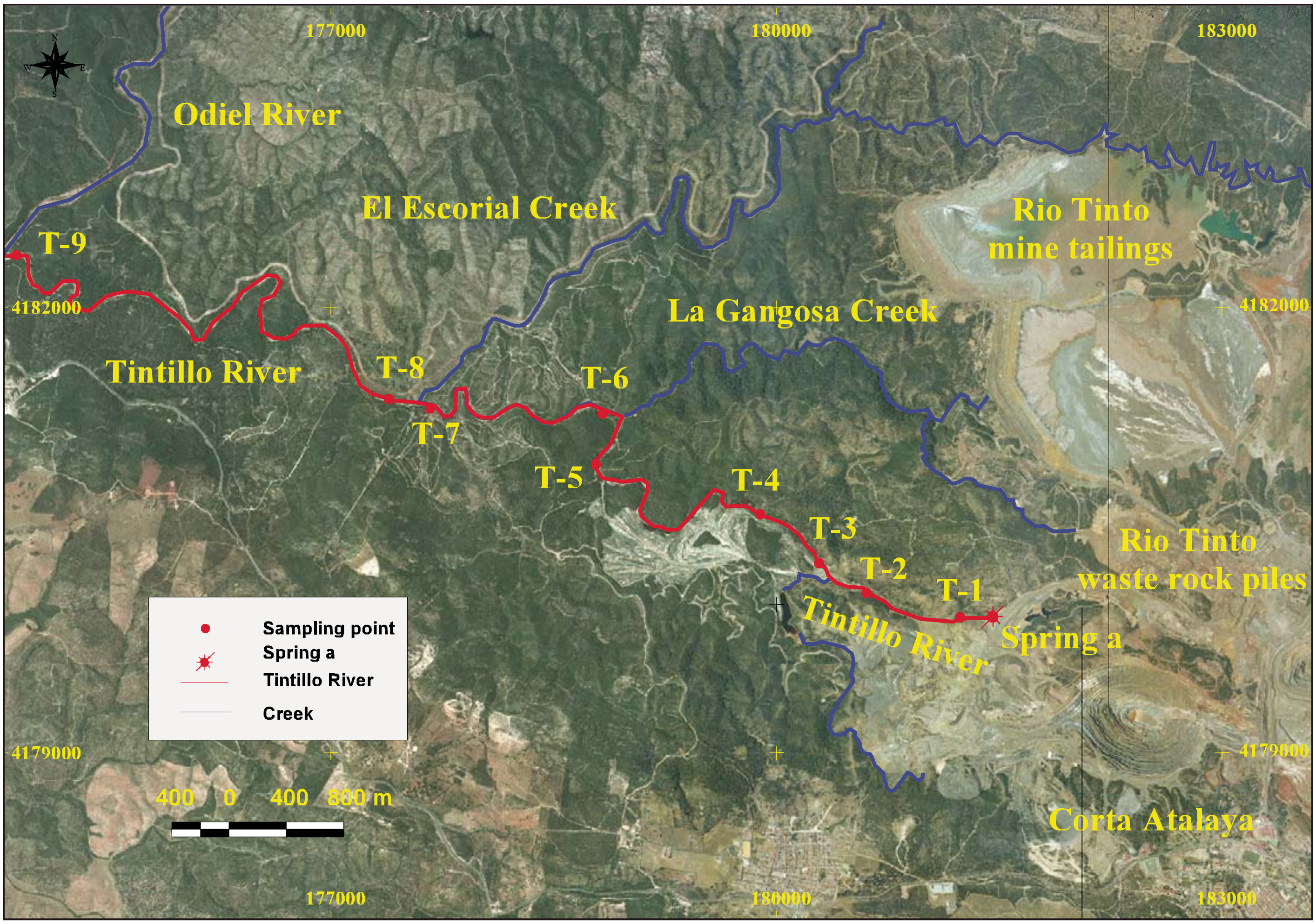

Figure 1. Configuration of the Tintillo acidic river (in red) and its main tributaries (in blue). For simplification, only spring a is shown in the source area. The locations of water and terraced iron formation (TIF) samples are also indicated.

water oxygenation and enhance the oxidation of Fe(II);

(3) abundant mat-forming, benthic communities of acidophilic, Fe-oxidizing bacteria, which have colonized the stream substrate and appear to enhance the oxidation of Fe(II);

(4) a considerable initial flow rate of between 15 and 30 L/s; and

(5) an initial pH around 2.6–2.8, which permits the hydrolysis/precipitation of aqueous Fe(III).

As a result of such favorable geochemical, hydrodynamic, and microbiological conditions, spectacular terraces of decametric scale have formed along the first 3.5 km of the river (Fig. 2).

The present study is aimed at providing further insight into the development of TIFs in acid mine drainage systems through preliminary hydrogeochemical, morphological, mineralogical, and microbiological findings from the exceptional Tintillo acidic river. Particularly, this work emphasizes the organic versus inorganic origin of these structures and presents results that include: (1) the chemical composition of the stream waters and its downstream evolution, (2) the major morphological, mineralogical, and chemical characteristics of the TIFs, and (3) the spatial (downward) evolution of living benthic microbes (algal and bacterial colonies) and their relation to the aqueous chemistry and TIF development. Finally, we hypothesize about the origin of TIFs by comparisons with similar acid mine drainage systems, as well as calcareous travertines formed in carbonate-rich environments.

ENVIRONMENTAL SETTING

Location and Hydrological Configuration of the Tintillo Acidic River

The Tintillo River is 10 km in length and drains an area of 57 km^2 in the northern part of Huelva province (Fig. 1). This river is mainly fed by leachates of acid mine drainage emanating from the base of large, sulfide-bearing, waste-rock piles and tailings impoundments situated in the surroundings of Corta Atalaya, a vast open pit exploited from 1907 to 1991 by the company Minas de Riotinto. At the headwaters of the river, there are a number of small acid mine drainage springs (named as spring a, spring b, etc.), which have variable flow rates on the order of a few liters per second and which finally converge in the T-1 sampling point (Sánchez-España et al., 2005c). Subsequently, the Tintillo River meets some tributaries (the Gangosa and Escorial creeks; Fig. 1), which are also acidic and show comparable flow rates but lesser sulfate and metallic content. Finally, the Tintillo River converges with the Odiel River, causing a strong environmental impact on the latter and a sharp decrease of its water quality (Sánchez-España et al., 2005c, 2006a).

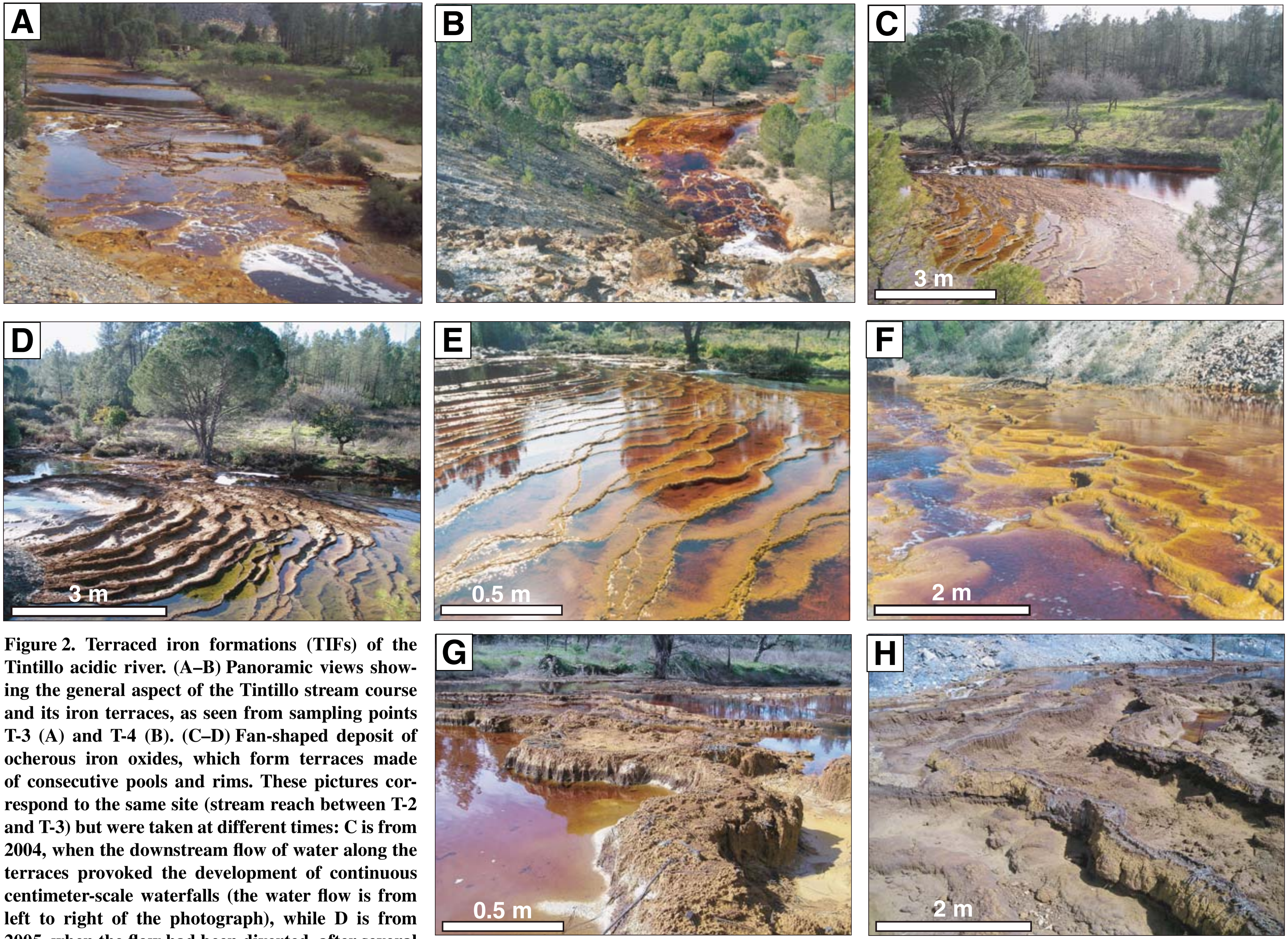

Figure 2. Terraced iron formations (TIFs) of the Tintillo acidic river. (A–B) Panoramic views showing the general aspect of the Tintillo stream course and its iron terraces, as seen from sampling points T-3 (A) and T-4 (B). (C–D) Fan-shaped deposit of ocherous iron oxides, which form terraces made of consecutive pools and rims. These pictures correspond to the same site (stream reach between T-2 and T-3) but were taken at different times: C is from 2004, when the downstream flow of water along the terraces provoked the development of continuous centimeter-scale waterfalls (the water flow is from left to right of the photograph), while D is from 2005, when the flow had been diverted, after several heavy rainfall events, to the left margin of the river, thus causing the abandonment of the terraces. At this point, the stream channel is around 15 m wide, and the pine tree in the center of the photo in D is ~8 m high. (E– F) Detail of the alternation of successive pools and rims in different points of the river (reach between samples T-2 and T-4); the channel width is around 15 m in E and around 8 m in F. (G– H) Abandoned, older terraces near T-3 (field of view is ~2 m wide in G and ~5 m wide in H). In contrast to the TIFs shown in A–F, which are mainly composed of schwertmanite (see also Fig. 6), the rims shown in G–H are mineralogically mature and have been transformed almost entirely to goethite (see also Fig. 7).

Morphological Description of the Tintillo Acidic River

For discussion purposes, three different sections along the Tintillo River were distinguished, namely: (1) an upper, Fe(II)-rich, nearly anoxic to oxygen-deficient pre-TIF section, (2) an Fe(III)-rich, suboxic TIF section, and (3) a post-TIF, oxygen-saturated, final section. These three sections differ in diverse aspects such as (1) water color and turbidity, (2) dissolved oxygen content, (3) Fe(II)/Fe(III) ratio of the acidic water, (4) oxidation/precipitation rate, (5) average flow velocity and stream section geometry, and (6) type of microorganisms colonizing the stream substrate.

Upper Section (Pre-TIF)

The upper section (first kilometer of the stream course, T-1 to T-2 in Fig. 1) is characterized by a narrow (50–90 cm wide) and shallow (5–10 cm deep) channel, with a steep slope and abundant, centimeter-scale falls, which favor oxygenation and the initial oxidation of Fe(II) to Fe(III). In this section, dissolved iron is mainly in reduced state (Fe[II] > 70% Fe_{total}; Sánchez España et al., 2005a, 2005c) and the acidic water is transparent (with a slightly greenish color), which favors the penetration of light into the water column. From a biological viewpoint, this segment is characterized by the presence of centimeter-thick, bright-green, filamentous biofilms at the discharge points of the acid mine drainage waters (Fig. 3). Precipitation of Fe(III) is minimal and no Fe-rich sediment is deposited on the stream bed.

TIF Section

From T-2 to T-5, the water is deep red in color, possibly due to the oxidation of Fe(II) and subsequent hydrolysis/precipitation of Fe(III) colloids in the water column, and the green biofilms are rarely observed because they are always restricted to the discharge points of anoxic, Fe(II)-rich acidic waters (Fig. 3D). In this section, the stream slope is more gentle, and the channel is notably wider (5–15 m), resulting in a significant decrease of the stream flow velocity. Spectacular iron terraces have formed on the stream bed, and they exhibit the typical morphology of a travertine-like, terrace deposit with a succession of gentle slopes and water falls (Fig. 2). These travertine-like deposits characterize the river morphology during most of its course, although they are especially abundant and strikingly developed in the stream reach between T-2 and T-5. In this segment, the ferruginous terraces can be up to 36 m long and close to 1 m deep, with surfaces made up of an alternation of meter-scale pool terraces and curved ridges structured transversely to the water flow. From a microbial perspective, this stream segment is characterized by submerged white

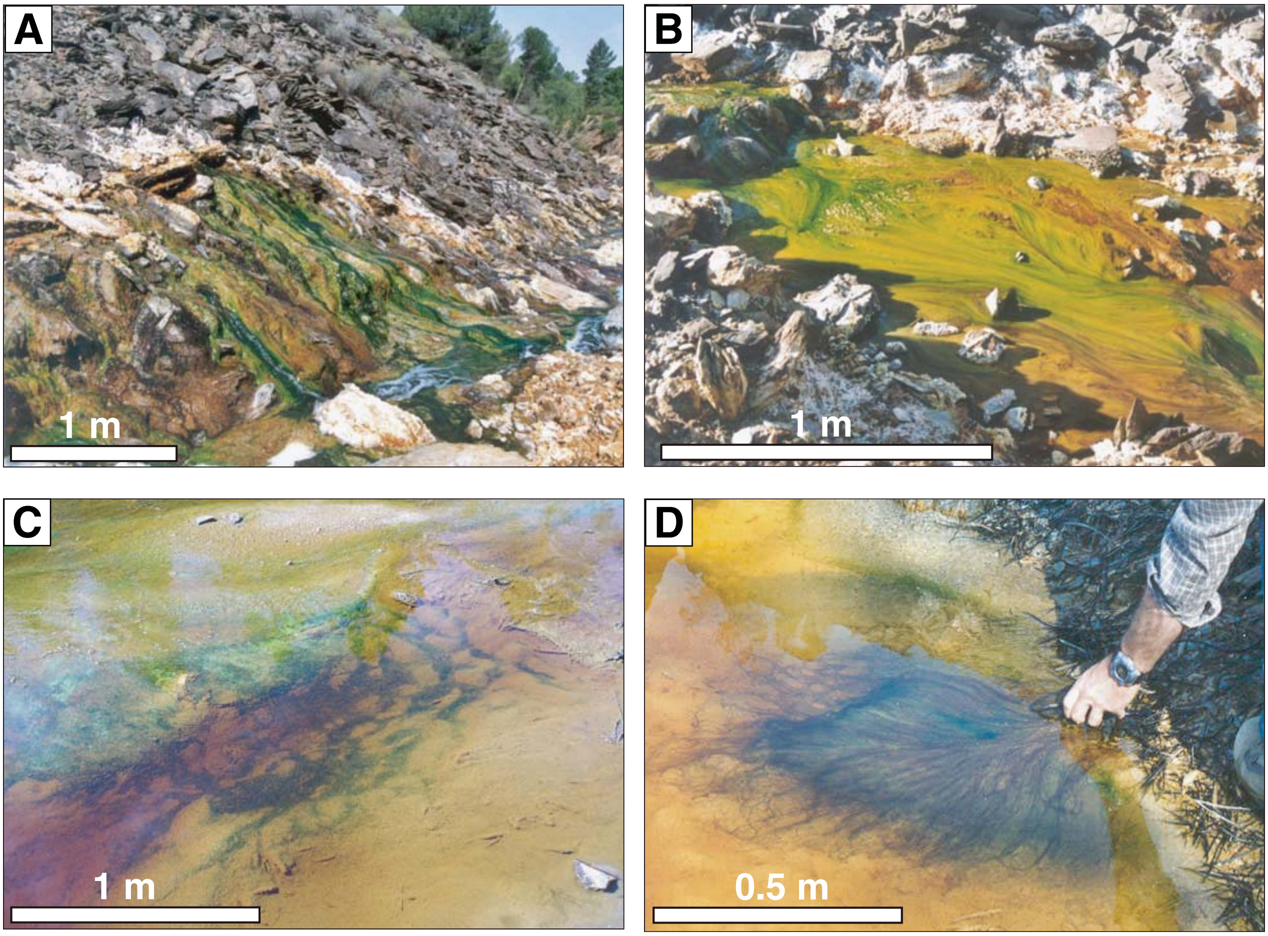

Figure 3. Photographs showing the aspect of the green filamentous biofilms that commonly colonize the source points of acidic waters. (A–B) Biofilms developed in spring a. (C) Biofilm colonizing the stream bed under a thin water layer between T-1 and T-2. (D) Fan-shaped colony of filamentous green algae growing outward from a discharge point of acidic, Fe(II)-rich, anoxic water near T-3.

streamers that are anchored to the sediments and especially cover the surfaces of the rims (ridges) of the terraces (see later section, "Filamentous, White Bacterial Streamers [TIF section]").

This aqueous-solid-biotic system is not static, and the appearance and configuration of the iron terraces can vary significantly with time. The terraces can be active (submerged and effectively growing upward) or abandoned, depending on the fluvial dynamics. For example, a collapse of part of a ridge during a rainstorm event with a subsequent sharp increase of the water flow can provoke a partial breakage of some terraces and the subsequent diversion of the stream from the active terraces to a separate margin, thus disconnecting temporally (or permanently) the terraces from the aqueous medium. Under such circumstances, the fresh ocherous precipitates are rapidly dehydrated and mineralogically evolved into more stable mineral phases such as goethite (Bigham et al., 1996; Nordstrom and Alpers, 1999; Sánchez-España et al., 2005a), and the mat-forming bacterial colonies disappear. This dynamic aspect of the TIFs has been observed during the last three years of study in the Tintillo acidic river, and it is illustrated in Figures 2C–2D.

Post-TIF Section

Downstream from T-5, the Tintillo River meets two tributaries (Gangosa and Escorial creeks), which are also acidic but less metal-enriched, and therefore they dilute the metal concentrations of the main stream (Sánchez-España et al., 2005a, 2005c). After having deposited massive terraces of hydrous iron oxides in the TIF section, and with most dissolved iron already oxidized (more than 70%–75% of the total iron being Fe[III]; Sánchez-España et al., 2005c; see also Table 1 in the next section), the water attains an apparent chemical equilibrium in this segment. At 4–10 km from the source area, the rates of Fe(II) oxidation and Fe(III) precipitation are significantly decreased with respect to the rates measured at the discharge point (Sánchez-España et al., 2007), and only thin terraces occur sporadically in the stream bed.

METHODS

Sampling

Water samples for chemical analyses of major ions and trace elements were taken in June 2003 and March 2004 with 60 mL syringes and Millipore standard sampling equipment, filtered on site with 0.45 µm membrane filters, stored in 125 mL polyethylene bottles, acidified down to pH < 2 with concentrated HNO_3, and refrigerated at around 4°C during transport. Additionally, solid samples ($n = 9$) of ocherous material were taken in June 2003 from the upper ridges (lips) of the terraces and were directly stored in 125 mL polyethylene bottles for the subsequent chemical and mineralogical (X-ray diffraction [XRD], scanning-electron–energy-dispersive microscopy [SEM-EDS]) analyses. For comparison, both the fresh terraces (submerged and actively forming) and older terraces (dry and isolated from the stream course) were sampled and analyzed.

Samples of green algal biofilms ($n = 3$) and white bacterial streamers ($n = 2$) were also collected from the stream substrate at different points along the studied course of the river. These samples were stored in 5% formaldehyde in 75 mL polyethylene bottles and studied under a petrographic microscope three days after collection.

Field Measurements and Laboratory Analyses

The analytical procedures for measurement of field parameters, chemical analyses of waters, as well as chemical and mineralogical (XRD-EDS) analyses of sediment samples have been previously described and can be found in Sánchez-España et al. (2005a, 2005b, 2006a, and 2006b).

Microscopic Study

The internal structure of the TIFs and the microbial communities that form the biofilms that cover the stream substrate were microscopically studied in a transmitted-light petrographic microscope (LEITZ) connected to a PHILIPS digital photographic camera. Polished thin sections were prepared from the terrace samples for the study of their sedimentary textures and microstructures. For the microbial study, cell suspensions were removed from the polyethylene bottles with a pipette and mounted on thin, transparent glass membranes to study their size and morphological characteristics.

Additionally, SEM images were taken and EDS analyses were carried out on minerals from bulk samples of the Fe-rich terraces with a JEOL JSM 6400 scanning electron microscope at UCM (Universidad Complutense de Madrid).

RESULTS

Hydrogeochemical Context of the TIFs

Chemical Composition of the Stream Waters

The main leachate feeding the Tintillo River at the source point (spring a; Fig. 1) is characterized by a pH of between 2.6 and 2.8, a relatively low redox potential (541–572 mV), and nearly complete anoxia (0.50–0.77 mg/L, 6%–10% sat.), in addition to very high concentrations of dissolved sulfate, iron (mostly ferrous), aluminum, and other metals (Table 1). The water composition for sample T-1 in June 2003 included 24,700 mg/L SO_4^{2-}, 1824 mg/L Fe, 2110 mg/L Al, 2830 mg/L Mg, 329 mg/L Mn, 557 mg/L Zn, and 184 mg/L Cu as major ions, in addition to 45,935 µg/L Co, 8546 µg/L Cd, 1107 µg/L U, 815 µg/L Cr, and 430 µg/L As, as most-significant trace elements (Table 1). This composition is relatively constant throughout the year, although it may experience slight temporal variations due to hydrological changes (alternation of dry summers, which provoke an increase in the concentration of sulfate and metals, with rainfall episodes more typical in winter and autumn, which tend to dilute the sulfate and metal contents; Table 1).

Previous calculations of saturation indices for selected minerals (Sánchez-España et al., 2005a, 2005b, 2005c) have shown that these waters are strongly oversaturated with respect to schwertmanite, which is the mineral favored to precipitate in most mine drainage settings in the pH range 2–4 (Bigham et al., 1996; Bigham and Nordstrom, 2000). These studies also indicated jarosite and goethite saturation, although these other ferric minerals are quantitatively less abundant than schwertmanite in the TIFs.

Bacterial Oxidation of Fe(II)

The acidic leachates that feed the Tintillo River (e.g., spring a; see Figs. 1 and 3) are practically anoxic in origin due to a strong oxygen demand for the bacterially mediated oxidation of pyrite and Fe(II) within the waste pile. After these effluents emerge in T-1 at 199 m downstream, the diffusion of atmospheric oxygen and the photosynthetic activity of green algal communities (see following) cause a rapid increase in the oxygen content to around 3.6–5.9 mg/L O_2 (~40%–70% sat.; Table 1). This O_2 subsaturation is maintained for 3500 m (T-5), and then O_2 level rises to near-saturation (89%–92% sat.) at ~4000 m (T-6). The subsaturation maintained along most of the TIF section is apparently due to an existing balance between (1) the bacterial consumption for Fe(II) oxidation, and (2) the oxygen gain either by diffusion from the atmosphere or by the photosynthetic activity of green algae and some other microbes, such as euglenophytes and diatoms. The oxidation of Fe(II) is evidenced by a fast and progressive decrease of the Fe(II) to total iron (Fe_{total}) ratio, which varies from 94% in spring a to 24% in T-5. Similarly, the Eh value, which is basically governed by the iron redox state, varies from 541 to 572 mV (typical of Fe[II]-rich waters) at the main source point (spring a), to values of 634–676 mV (characteristic of more oxidized aqueous environments

TABLE 1. DOWNSTREAM VARIATION OF PHYSICO-CHEMICAL PARAMETERS—pH, REDOX POTENTIAL Eh, DISSOLVED OXYGEN (DO), PERCENT PROPORTION OF FERROUS TO TOTAL IRON (FE[II]/FE$_{total}$), WATER FLOW (*Q*) —AND AQUEOUS CHEMICAL COMPOSITION ALONG THE COURSE OF THE TINTILLO ACIDIC RIVER IN JUNE 2003 AND IN MARCH 2004

Sample units	Distance (m)	*Q* (L/s)	pH	Eh (mV)	DO (%)	Fe(II)/Fe$_{total}$ (%)	SO$_4$ (g/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Al (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Cu (mg/L)	Zn (mg/L)	As (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Pb (µg/L)	Th (µg/L)	U (µg/L)
June 2003																							
spring a	0	6	2.8	541	5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
T-1	199	15	2.6	573	44	–	24.7	13.9	0.93	236	2107	1824	2833	329	184	557	430	8546	45,935	815	<10	389	1107
T-2	910	15	2.5	591	56	–	24.6	13.8	0.21	234	2135	1847	2886	333	188	574	525	8075	45,564	776	14	413	1142
T-3	1294	25	2.5	597	47	–	24.2	15.1	0.26	233	2032	1689	2659	317	179	545	1369	7197	38,160	706	18	404	1093
T-4	1817	30	2.5	617	49	–	18.6	18.0	0.40	202	1453	1135	2011	241	136	394	233	1970	8902	219	9	126	339
T-5	3503	30	2.3	634	60	–	18.3	19.1	0.29	208	1516	999	1854	251	133	373	137	1719	7929	217	12	130	338
T-6	3993	60	2.4	657	92	–	14.1	69.8	3.65	199	993	854	1427	175	135	273	212	984	5362	121	38	89	216
T-7	5602	60	2.3	657	92	–	14.8	69.2	3.81	207	969	791	1372	167	132	264	169	957	5670	103	39	89	209
T-9	10,035	60	2.1	699	86	–	13.8	75.4	3.56	218	958	674	1367	170	137	267	63	982	6172	118	45	101	220
March 2004																							
spring a	0	10	2.6	572	6	94	26.59	12.6	0.22	150	2003	1686	2521	211	145	450	54.2	954	17,507	115	<10	102	313
T-1	199	28	2.6	606	68	71	23.91	12.5	0.15	148	1990	1751	2638	206	157	461	241	874	16,046	116	<10	163	322
T-2	910	31	2.8	616	47	66	22.64	11.2	0.14	148	1577	1762	2586	201	156	457	237	841	14,909	114	16.9	157	305
T-3	1294	52	2.8	624	58	53	21.67	11.5	0.15	145	1492	1567	2416	192	145	429	300	795	13,780	105	12.3	150	293
T-4	1817	73	2.8	636	67	51	19.85	12.9	0.25	135	1174	1248	1971	172	129	389	194	483	9721	86	12.3	129	249
T-5	3503	78	2.8	676	–	24	15.52	14.4	0.38	127	1105	963	1695	151	107	316	152	440	7827	82	14.8	107	202
T-6	3993	152	2.8	665	89	31	11.44	53.2	2.54	123	839	716	1183	109	134	223	231	436	7780	51	31	74.2	121
T-7	5602	276	2.9	678	97	26	6.89	51.0	2.67	118	457	353	663	65.3	70.2	129	90	325	4110	29	31	38.4	65
T-9	10,035	313	2.8	685	94	25	6.92	49.8	2.38	113	422	293	613	61.2	65.32	119	59	186	3456	26	35	38.3	63

with dominant Fe[III]) at the end of the TIF section (T-5). Further downstream, Fe(II) is mostly oxidized (Fe[III] > 75% Fe$_{total}$) and the water becomes nearly O$_2$-saturated (Table 1).

The field determinations of Fe(II)/Fe(III) concentrations in different sampling points along the Tintillo stream course (Table 1), along with the calculation of the residence time of water between successive stations, have made it possible to roughly estimate the average field rate of bacterial oxidation of Fe(II) and its evolution in a downstream direction (Fig. 4). From these estimations, we conclude that Fe(II) is being oxidized at rates of between 2 mmol L^{-1} h^{-1} (pre-TIF and TIF sections) and 0.1 mmol L^{-1} h^{-1} (post-TIF section). As a result of such rates of microbial oxidation, ~34% of the ferrous iron initially dissolved in spring a had already been oxidized to Fe(III) at only 910 m from the river source (Table 1; Fig. 4). These rates are characteristic of bacterially catalyzed oxidation (Stumm and Morgan, 1996; Nordstrom and Alpers, 1999) and provoke the appearance of dissolved and particulate Fe(III), which turns the acidic waters a deep red color. The different oxidation rate of the TIF section with respect to the rest of the stream course may represent indirect evidence of a different density of bacterial populations existing in these different sections of the river (Sánchez-España et al., 2007). In the TIF section (first 3.5 km), thick layers of bacterial biofilm are conspicuously developed over the stream substrate, whereas the occurrence of these bacterial mats is much less significant beyond the confluence with the Gangosa acidic creek, which could also represent an important dilution of the planktonic bacteria present in the water column.

Textural, Mineralogical, and Chemical Features of the TIFs

Both macroscopically and microscopically, the iron terraces commonly present a rough lamination consisting of thin, wavy laminae and thicker, porous, sponge-like layers (Figs. 5C–5D, 6A–6B, 7C–7D). In addition to this macroscopic arrangement, under the transmitted light microscope, a finer lamination can be observed, alternating very fine-grained, highly porous, light orange laminae with more massive, dark orange to brown layers (Figs. 6C–6D). The difference between these bands may be defined either by the grain size (the lighter laminae are mainly composed of very fine-grained crystals and/or colloidal particles, and the darker layers show a more massive and coarse-grained arrangement; Figs. 6C–6D), or by the internal structure of the respective bands (the lighter layers show organically derived structures, such as radiating fibers that resemble bacterial streamers, and the darker layers show abundant colloform and euhedral textures typical of crystalline growth; Figs. 6E–6F). It is worth noting that such internal arrangement is usually preserved during the dehydration and mineralogical maturation of the terraces, so that the more crystalline layers rich in schwertmanite are converted to goethite, and the more porous, sponge-like layers are normally transformed into plume-like structures, which appear to be mineralized organic structures (Fig. 7). Whether the latter structures correspond to former bacterial colonies (streamers) or not is yet to be established, although this possibility seems more than probable. In other instances, the iron terraces are internally massive and do not show lamination.

Overall, the majority of the volume is occupied by a mixture of ocherous minerals (70%–80%), fallen pine leaves (10%–20%), which are normally cemented by hydrous iron oxides, some detritic silicates (quartz and muscovite, <5%), and gypsum (<5%) as authigenic mineral filling voids (Fig. 8). The XRD analyses indicated that the hydrous iron oxides consist mostly of schwertmanite, which is a hydroxysulfate of Fe(III) with very low crystallinity that typically forms in acid mine drainage settings (Bigham et al., 1996). This mineral forms very fine spherulite-shaped particles that are commonly aggregated together, thus forming a poorly cohesive chemical sediment (Figs. 6A–6C). In addition to schwertmanite, other iron oxides like jarosite and goethite were also observed within the TIFs (Table 2). Jarosite is distinguished from schwertmanite by its light orange to yellow color and its more crystalline, euhedral habit (Fig. 8C), whereas goethite is dark red to brown in color and forms botryoidal growths (Fig. 7). These three minerals rarely coexist as precipitating minerals, since jarosite is favored to precipitate under very acidic conditions (i.e., pH < 2–2.5), whereas goethite is usually a product of mineral maturation (recrystallization of schwertmanite and jarosite) rather than a directly precipitated phase (Bigham et al., 1996; Bigham and Nordstrom, 2000; Sánchez-España et al., 2005a). In fact, schwertmanite is a metastable phase that tends to be transformed into goethite upon dehydration and mineralogical maturation or diagenesis (Bigham et al., 1996). An evidence of this mineralogical evolution consists of the observation that goethite is rarely present in fresh (submerged and actively forming) terraces (Figs. 2C, 2E–2F, 6A–6F; Table 2), while it is the dominant mineral (confirmed by XRD and EDS analyses) in ancient terraces that have been abandoned by the fluvial dynamics (Figs. 2D, 2G–2H, 7A–7D).

Another typical occurrence of schwertmanite observed in the field is in the form of very thin layers or films floating on the water surface in low-flow or stagnant sites of the river (Fig. 5E–5F; Sánchez-España et al., 2005a, 2006b). These schwertmanite layers are characteristic of the dry (summer) season, and usually include fibrous to concentric forms. Although these layers have not been studied in detail, we hypothesize that they could be the result of mineral precipitation provoked either by (1) preferential oxidation of Fe(II) around the cells of neustonic microbes, which would serve as nucleation sites for these authigenic Fe(III) phases, and/or (2) oversaturation induced by intense evaporative processes taking place on the water surface. Regarding the first possibility, the presence of important neustonic communities composed of large amounts (10–100 times the concentration observed in the water column) of algae, fungi, protozoans, and bacteria at the water surface has already been reported in the adjacent Tinto River (López-Archilla et al., 2004a; López-Archilla, 2005). Some of the bacteria recognized in these communities (γ-Proteobacteria such as *Pseudomonas*) have pigments that actively sequester Fe(III) from the water (López-Archilla et al., 2004a; López-Archilla, 2005). Moreover, the bioaccumulation of iron on the cell surfaces of protozoans and bacteria either by enzymatic or nonenzymatic processes has been already reported (Ehrlich, 2002). Whatever their actual origin might be, these Fe(III) films also contribute to the formation of TIFs, since they usually thicken and sink after some time, thus coarsening the pools of the iron terraces (this process was frequently observed in the field during the summer season).

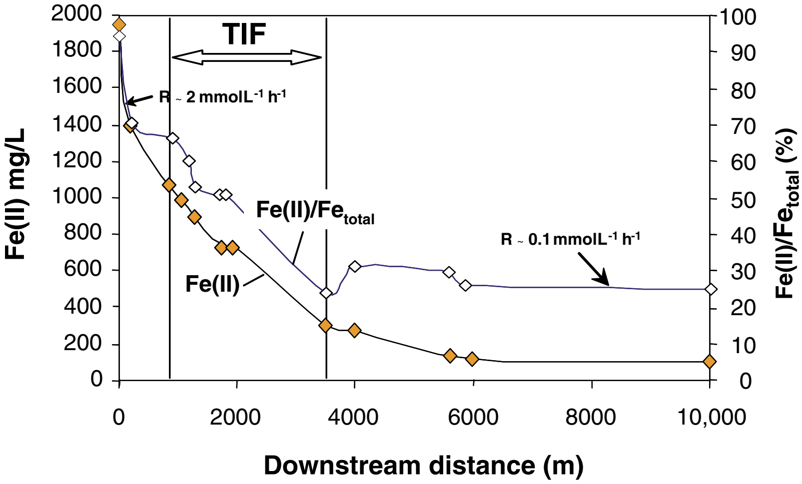

Figure 4. Downstream evolution of the ferrous iron (Fe[II]) and ferrous to total iron ratio (Fe[II]/Fe$_{total}$) along the Tintillo acidic river (from spring a to T-9; Table 1). TIF—terraced iron formation. R—apparent reaction rate for Fe (II) oxidation.

The chemical composition of the TIFs (Table 2) is coherent with their mineral composition, with average contents of around 60% of Fe_2O_3 and volatile content (LOI) of around 32%, which are similar to those measured in monomineralic schwertmanite (Bigham et al., 1996; Sánchez-España et al., 2005a). In addition, very variable contents of silica (0.1%–21.4%) and alumina (1.1%–5.6%) are also present depending on the amount of detritic silicates in the samples. These solids also contain significant concentrations of As (190–1369 ppm) and trace metals like Mn (0.04%–0.08% as MnO), Cu (340–1107 ppm), Pb (107–799 ppm), and Zn (71–442 ppm), which could have been adsorbed onto the mineral surfaces of the Fe(III) solids during precipitation (Table 2).

Microbial Evolution along the Stream Substrate

A detailed classification of the benthic communities of microbes of the Tintillo River is beyond the scope of this work. However, a clear transition of these microorganisms has been observed along the stream channel (green filamentous algae dominating in the first meters of the river course near the source point, euglenophytes and diatoms dominating in the intermediate section, and bacterial streamers characterizing the TIF section). This observation has strong implications for the discussion on the development of TIFs, and so a brief field and microscopic description of these acid mine drainage–related microbes is given below.

Filamentous, Green Algae–Dominated Biofilm (Discharge Points)

The sources of the acidic waters at the bottom of the waste piles and tailings are always

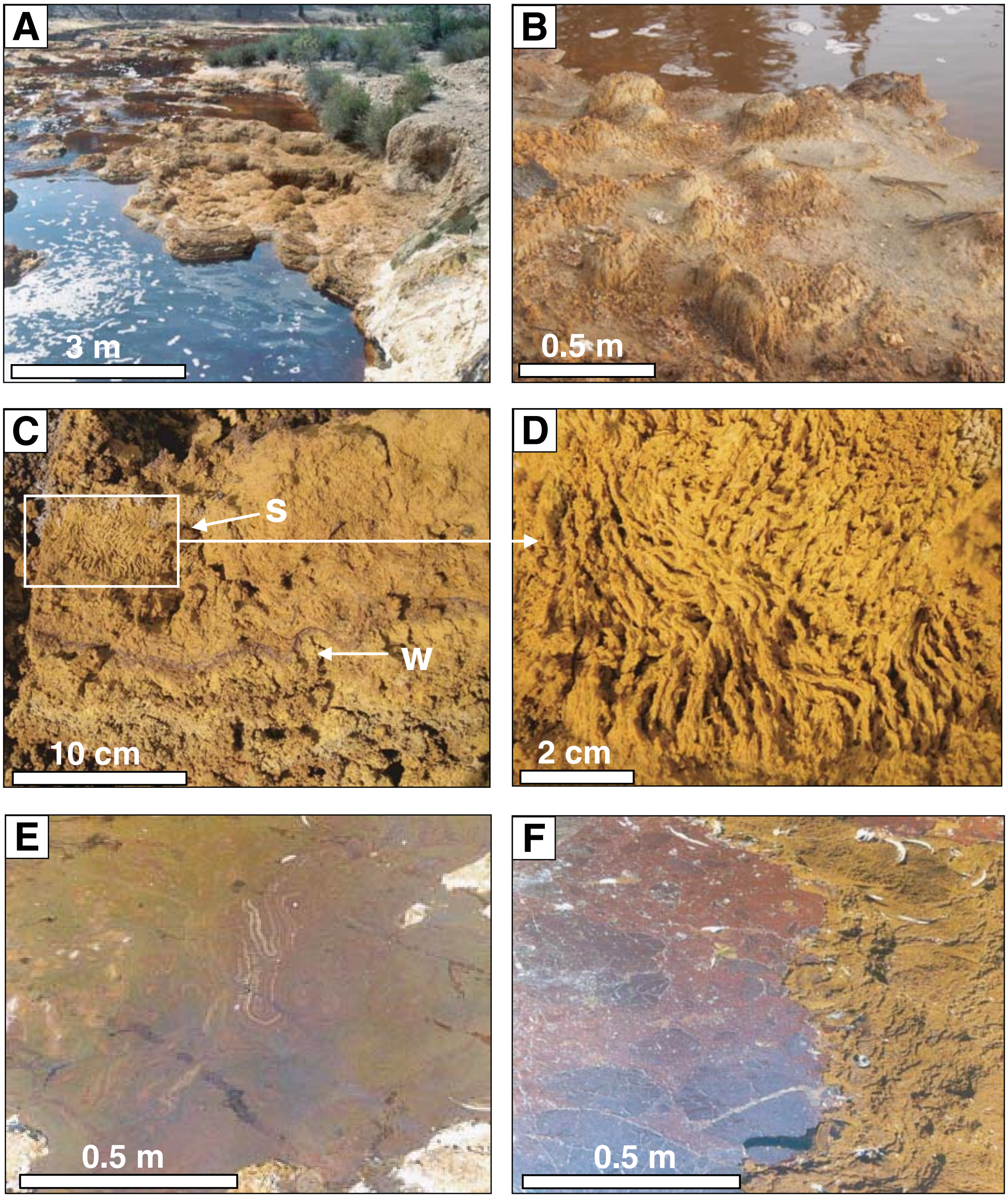

Figure 5. Field evidence of microbial activity in the Tintillo River. (A–B) Mound-shaped structures formed under subaqueous conditions, but presently emerged and abandoned by the main stream course. Reach is between stations T-2 and T-3 (field of view is ~8 m wide in A and around 2 m wide in B). (C) Internal lamination of the terraced iron formations, with alternation of wavy (w) and sponge-like (s) layers (field of view is ~30 cm). (D) Detail of the internal structure observed in the spongy layers (upper left corner in C) with subvertical, radiating growths of probable microbial origin (former bacterial streamers ?) (field of view is 8 cm). (E– F) Ocherous film floating on the water surface near T-2. The identification of this layer by X-ray diffraction (see Figure 7, p. 1339, in Sánchez-España et al., 2005a) revealed that it is basically made of schwertmanite, although the internal structure of the film includes geometric patterns that may suggest mineral nucleation and/or precipitation around neustonic microbes.

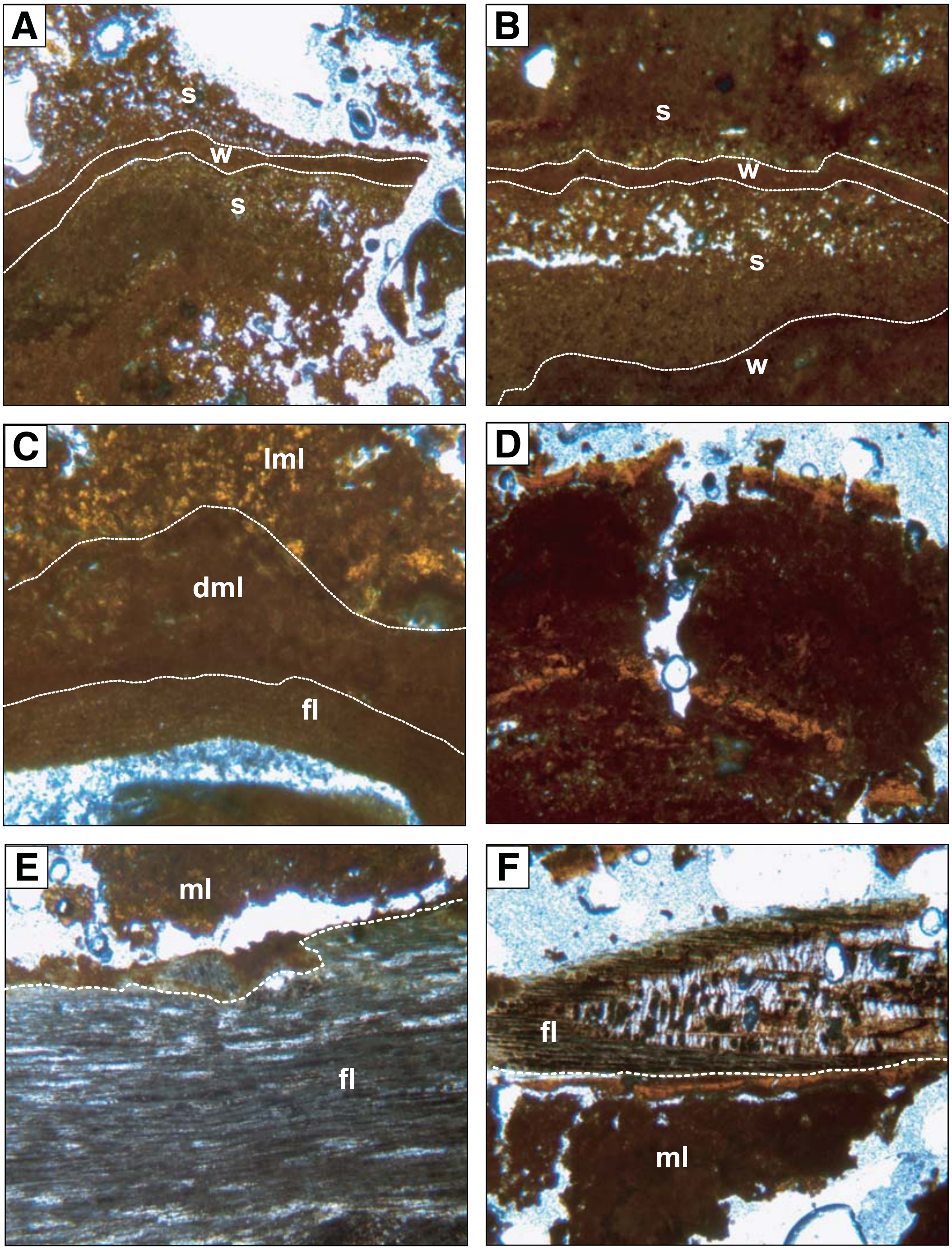

Figure 6. Microtextural evidence of lamination in the young (fresh and currently forming) terraces of the Tintillo River (see Figs. 2E–2F). (A–B) Alternation of spongy (S) and wavy (W) layers within the terraced iron formation (TIF). (C) Fibrous layer (fl) of possible microorganic origin, above which mineral crystallization has taken place, showing evidence of a light mineral layer (lml) that has grown onto a dark mineral layer (dml). (D) Microstromatolite-like mineral growth, showing an alternation of thicker, dark brown layers with thinner, light orange layers. (E–F) Mineral layers (ml) alternating with fibrous layers (fl) of probable organic origin. All photomicrographs were taken in a petrographic microscope under plane polarized light with a 20× objective adjusted to a digital camera mechanism; the field of view is ~2 mm across in all cases.

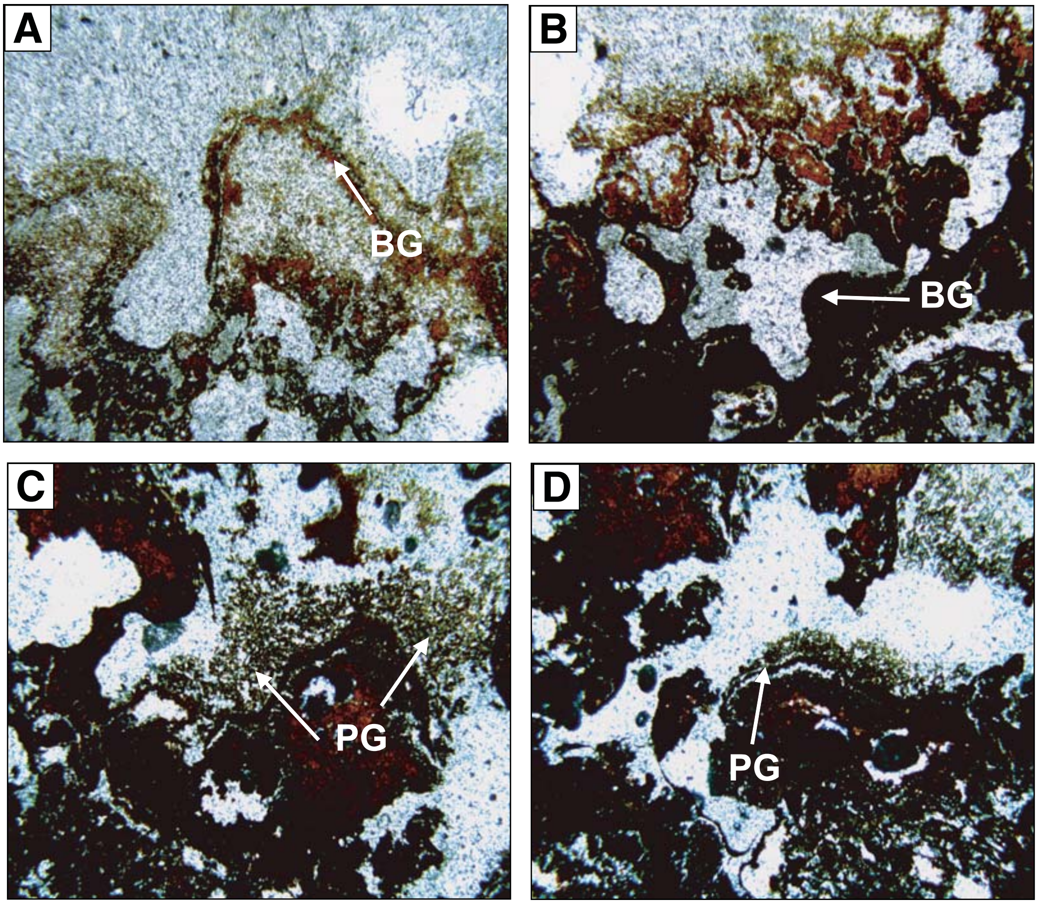

Figure 7. Microtextural evidence of lamination in the aged (desiccated and mineralogically evolved) terraces of the Tintillo River (see Figs. 2E–2H). (A–B) Botryoidal growths (BG) of goethite (the presence of this mineral was confirmed by energy-dispersive spectrometry [EDS] and X-ray diffraction [XRD] analyses). The background, clear material is the epoxy used for the preparation of the thin sections. (C–D) Plume-like growths (PG) forming on the crystalline edges of the concentric and botryoidal growths of goethite. All photomicrographs were taken in a petrographic microscope under plane polarized light with a 10× objective adjusted to a digital camera; the field of view is ~4 mm across in all cases.

colonized by bright green, submerged algal biofilms. These biofilms cover as much as 100% of the stream substrate during the first meters from the discharge points, can be up to several millimeters thick, and serve in the field as biomarkers of anoxic, Fe(II)-rich acid mine drainage emissions (Fig. 3). The bright green color shown by these algae denotes the presence of chlorophyll, and the photosynthetic activity of these microorganisms is evidenced by the presence of oxygen bubbles at the water-air interface (Fig. 9A). This photosynthetic oxygen production provokes locally oxygen-rich aqueous conditions, which are especially important for the enhancement of the bacterial oxidation of Fe(II).

Under the microscope, these microorganisms consist of single, elongated squared cells of around 5–6 μm in diameter that are attached side by side, forming very long filaments up to 200–300 mm in length (Figs. 9B–9C). The cells show a single membrane that encloses a green-colored cytoplasm and commonly includes orange to dark brown–colored granules extracellularly attached to their surfaces. These morphological features are common to algae of the phylum Chlorophyta, which have been widely observed in the adjacent Tinto River (including *Klebsormidium*, *Zygnema*, *Chlorella*, or *Chlamydomonas acidophila*; López-Archilla and Amils, 1999; López-Archilla et al., 2004b), where they represent the primary producers of the microbial community.

Although these photosynthetic algae are dominant at the discharge points, white streamers probably consisting of Fe-oxidizing bacteria are also observed, either below the algal mats and/or intergrowing with the algal filaments, suggesting a close association between both types of microorganisms.

Diatom- to Euglenophyte-Dominated Biofilm (Pre-TIF Section)

From a microbiological perspective, the section of the river between the source point and the beginning of the TIFs (T-2) is characterized by a mixed microbial community that is mainly composed of euglenophytes, diatoms, and bacteria (Fig. 10A). Macroscopically, this biofilm is stratified and includes three different layers: (1) an upper layer made up of isolated patches of brown to olive green color, which can be either entwined or randomly distributed over the second layer, (2) an intermediate layer of bright green, massive mats, and, finally, (3) a bottom layer of filamentous, white streamers, which are immediately above the stream substrate.

Microscopic examination of this biofilm has shown that the brown to olive green patches are colonies of diatoms (Figs. 10B–10C), whereas the bright-green, massive biofilm is mainly composed of euglenophytes (Figs. 10D–10E). The diatoms, which are tabular in shape and around 5–10 μm in length, have been observed to be a major contributor to the algal biomass of the Tinto River (López-Archilla and Amils, 1999) and to other Fe-rich stromatolite that form in acid mine drainage systems (Brake et al., 2004). The euglenophytes are present as elongated cells of around 5 μm in length, with a rounded end of the cell showing a characteristic red stigma (eyespot), and a thinner opposite end. Abundant chloroplasts separated by colorless areas are distributed along the cells. This morphology is similar to that described for the euglenophyte *Euglena mutabilis*, a well-known acidophilic, photosynthetic protozoan that contributes to the formation of Fe-rich stromatolites in acid mine drainage systems (Brake et al., 2001, 2002), and has been described in the adjacent Tinto River (López-Archilla et al., 2001, 2004b; López-Archilla, 2005). Directly

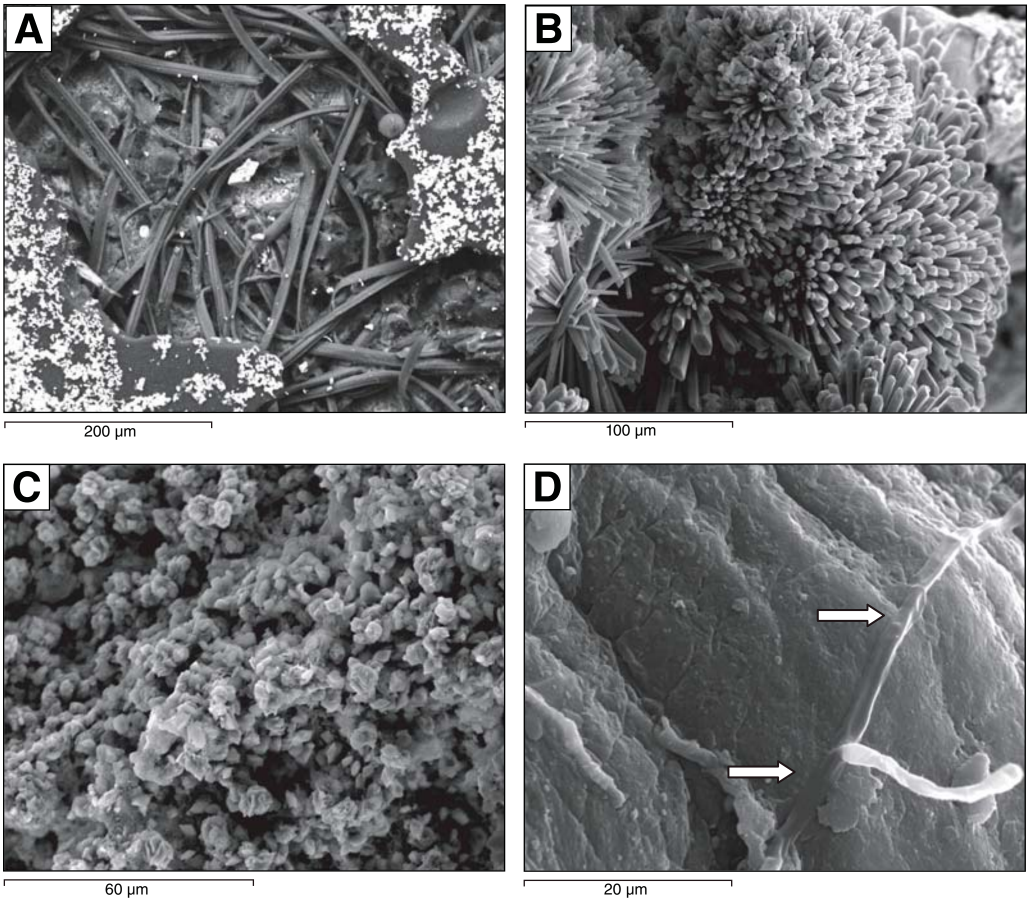

Figure 8. Scanning-electron microscope (SEM) images showing some typical elements of the internal structure of the terraced iron formations. (A) Detail of pine leaves cemented by iron oxides. (B) Radial growths of authigenic gypsum crystals, which form efflorescences in most of the voids. (C) Euhedral crystals of jarosite, which are aggregated and form a coherent chemical sediment. (D) Detail of fungal hyphae (white arrows), which are also common as trace constituents of the terraced iron formations (TIFs).

below the euglenophyte layer, there exists a thin undermat of white bacterial streamers.

Filamentous, White Bacterial Streamers (TIF Section)

This section is characterized by the scarcity to almost virtual absence of green algae, diatoms, and euglenophytes, and the conspicuous presence of thick (up to 1 cm), white filamentous streamers that cover the rims of the Fe-rich terraces immediately below the water surface (Figs. 11A–11B). Under the microscope, these streamers are chiefly composed of rod-shaped bacterial cells of <1–2 μm in length, although fungal hyphae with variable lengths are also commonly observed in association with bacteria (Fig. 8D). Important fungal populations have been also described in the Tinto River by López-Archilla et al. (2004a). The bacterial cells are densely packed and entwined with one another, forming strongly cohesive mats (Fig. 11). Although no distinction of bacterial species has been made, the observed macro- and microscopic features of the streamers resemble those described by other researchers for mat-forming colonies of Fe-oxidizing bacteria in which *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* have been recognized (e.g., López-Archilla and Amils, 1999; González-Toril et al., 2003; López-Archilla, 2005).

DISCUSSION

"Fe-Stromatolites" Formed in Acid Mine Drainage Systems: The Microbial Perspective

Although at a more minor scale than in the Tintillo River, similar iron formations composed of laminated terraces have been also described in association with living microorganisms in the Green Valley coal mines, Indiana, USA (Brake et al., 2001, 2002, 2004), and in the Carnoulés Pb-Zn mine in Gard, France (Leblanc et al., 1996). In these sites, the observed microbes have been considered to be the origin of the iron terraces, which could thus represent modern analogs of the ancient banded iron formations (BIF), and even Precambrian stromatolites. These acid mine drainage–related iron deposits meet all the criteria to be considered as modern stromatolites in the sense that they are accretionary, organosedimentary structures produced by sediment trapping, binding, and/or precipitation as a result of the growth and metabolic activity of mat-forming microorganisms (Walter, 1976; Awramik et al., 1976). However, there is an important difference between these two acid mine drainage stromatolite systems in the type of microbial communities involved in their formation. Thus, Brake and co-workers found textural, sedimentary, and microbiological evidences to conclude that the Fe-rich stromatolites of the Green Valley coal mines are, in part, the result of the photosynthetic activity of eukaryotic cells, specifically euglenophytes, such as *Euglena mutabilis*, and diatoms, such as *Nitzschia tubicola* (Brake et al., 2001, 2002, 2004). These protists contribute to the formation of the Fe-stromatolites either directly (by intracellularly storing Fe compounds released after death) or indirectly (by generating O_2 via photosynthesis that enhances the oxidation of Fe[II] and subsequent inorganic precipitation of Fe[III] minerals; Brake et al., 2001, 2002, 2004). On the other hand, according to Leblanc and colleagues, the As-rich ferruginous accretions of the Carnoulés Pb-Zn mine are the result of the cyclic development of bacterial colonies (including *Acidithiobacillus ferrooxidans*, *Acidithiobacillus acidophilus*, and other heterotrophic bacteria of the genus

TABLE 2. MINERALOGICAL AND CHEMICAL COMPOSITION OF THE Fe-RICH TERRACES OF THE TINTILLO ACIDIC RIVER (SAMPLE NUMBERS AS IN TABLE 1)

Sample no.	Mineralogy	Major oxides											Trace metals			
		SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MnO	K_2O	MgO	Na_2O	P_2O_5	LOI	Total	As	Cu	Pb	Zn
P-T-1	Jar, Goet, Qtz	5.30	1.74	60.31	0.15	0.32	0.06	0.26	0.25	0.14	0.21	31.04	99.76	860	1107	406	442
P-T-2	Schw	1.78	1.35	58.40	0.11	0.41	0.06	0.10	0.21	<0.1	0.20	37.34	99.96	709	421	297	383
P-T-3	Schw, Qtz	3.83	2.47	55.33	0.17	0.24	0.08	0.28	0.52	<0.1	0.22	37.00	100.14	1114	393	222	418
P-T-4	Schw, Qtz	3.40	1.82	58.36	0.11	0.20	0.06	0.26	0.15	<0.1	0.14	35.81	100.30	818	435	236	286
P-T-5	Qtz, Mc, Jar	19.60	5.35	50.32	0.06	0.28	0.05	1.03	0.23	0.23	0.17	22.97	100.30	998	633	221	135
P-T-6	Goet, Schw, Qtz	2.82	1.50	63.95	0.10	0.11	0.05	0.18	<0,10	<0.1	0.15	31.14	99.99	794	814	107	212
P-T-7	Jar, Goet, Qtz	4.45	1.96	60.35	0.07	0.10	0.04	0.47	<0,10	0.34	0.11	32.38	100.25	1369	930	386	122
P-T-8	Qtz, Schw, Mc	21.45	5.61	43.75	0.36	0.45	0.05	0.81	0.25	0.39	0.22	26.45	99.78	1043	697	799	341
P-T-9	Schw	0.10	1.13	63.73	0.12	0.01	0.05	0.10	0.10	0.07	0.04	34.86	100.30	190	340	–	71

Note: Only the minerals detected by X-ray diffraction (XRD) are reported. Major oxides are in wt%, and trace elements are in ppm. Mineral abbreviations: Schw—schwertmanite; Jar—jarosite; Goet—goethite; Qtz—quartz; Mc—muscovite. LOI—loss on ignition.

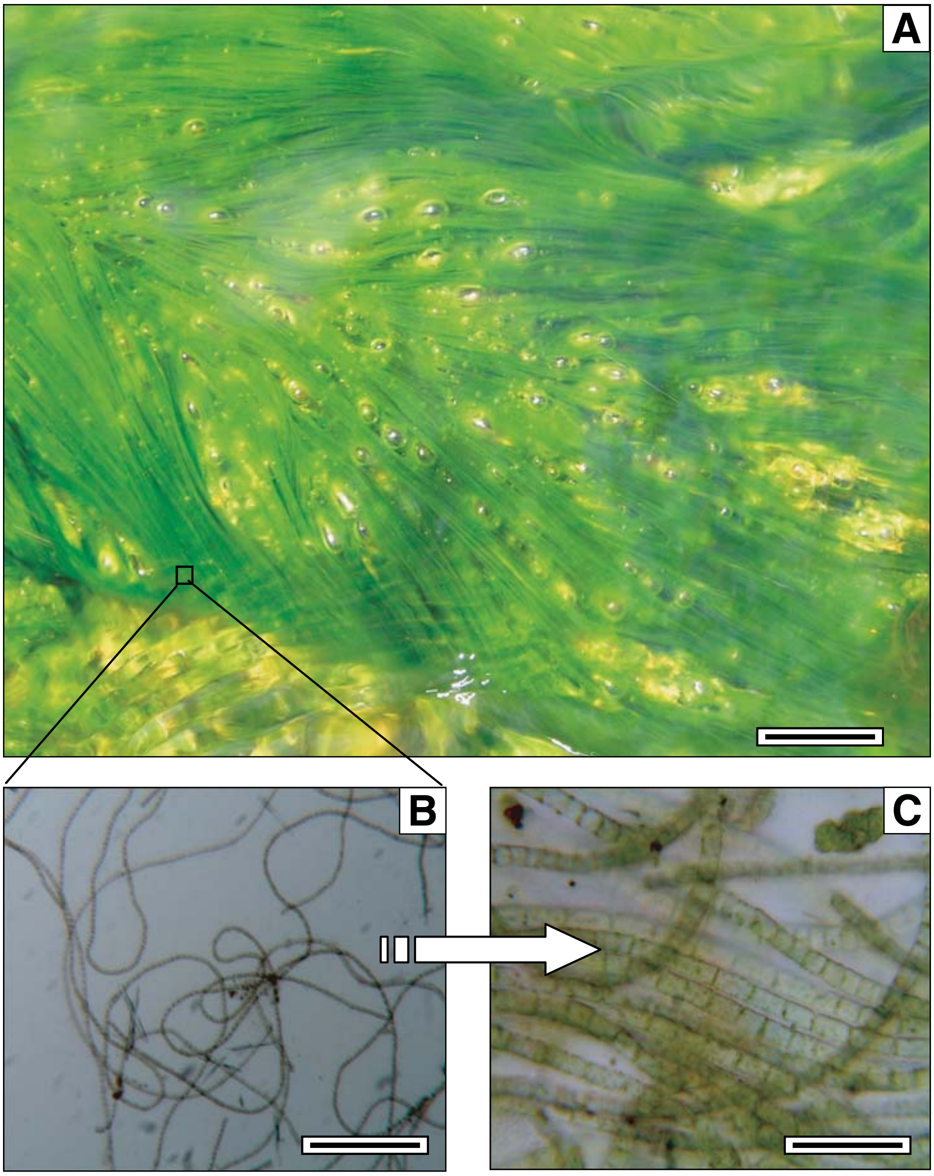

Figure 9. Field and microscopic aspect of the green, filamentous biofilm that has colonized the T-1 site. (A) Field view of the algal filaments anchored to the sediments (note the abundant oxygen bubbles formed by photosynthetic activity); the scale bar represents 2 cm. (B) Microscopic aspect (under transmitted light petrographic microscope) of the long algal filaments that form the biofilm (scale bar is 200 µm). (C) Detail of the algal cells, which are entwined with one another and form long filaments; the green color of the cells is caused by the chlorophyll contained within the cytoplasm; scale bar is 20 µm.

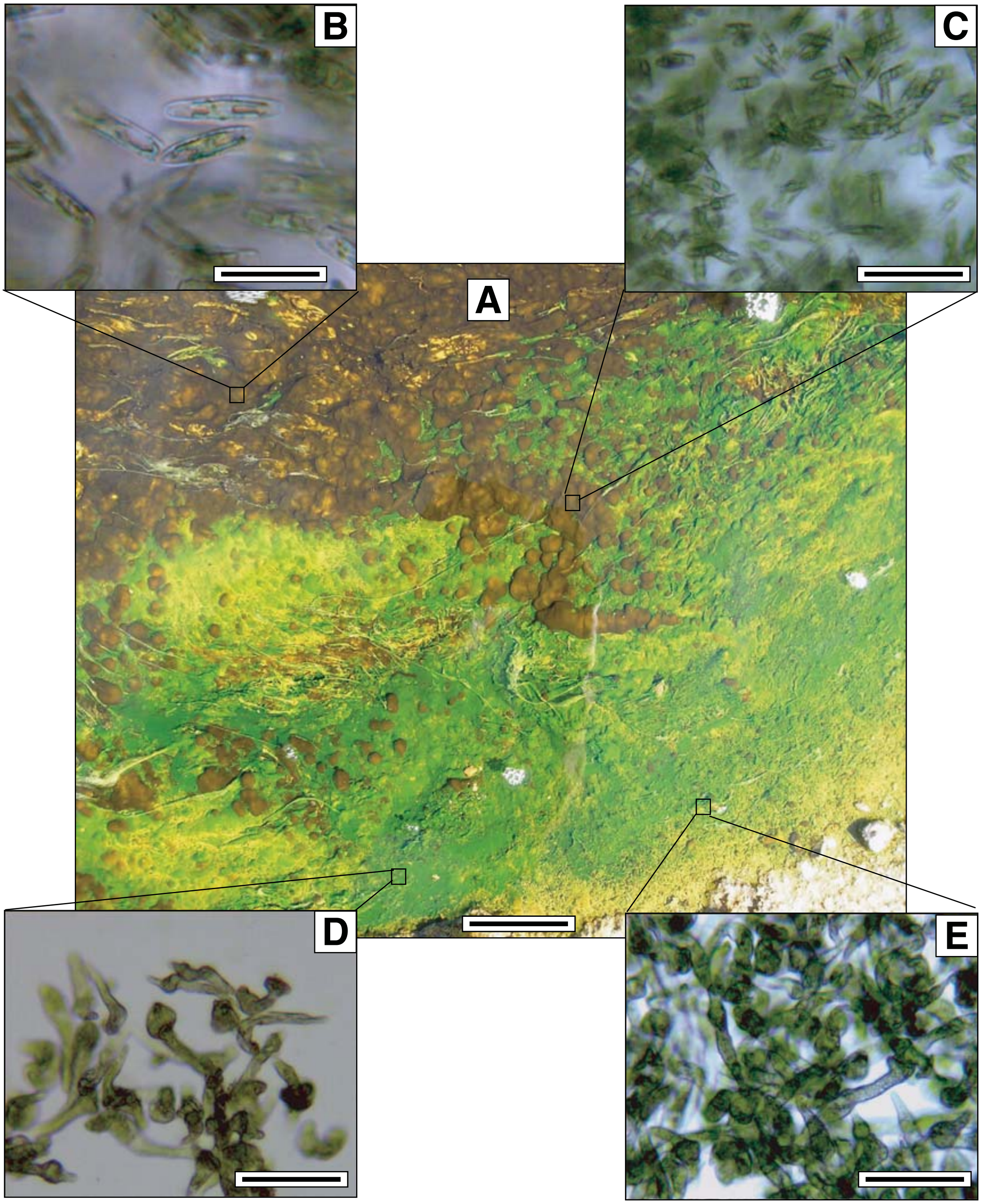

Figure 10. Field and microscopic aspect of the diatom- to euglenophyte-dominated biofilm that has colonized the stream substrate between T-1 and T-2 (pre-TIF section). (A) Field aspect (the scale bar represents 2 cm). (B–C) Microscopic aspect (under transmitted light petrographic microscope) of the diatoms (scale bars are 5 µm). (D–E) Microscopic aspect of the euglenophytes (scale bars are 5 µm). TIF—terraced iron formation.

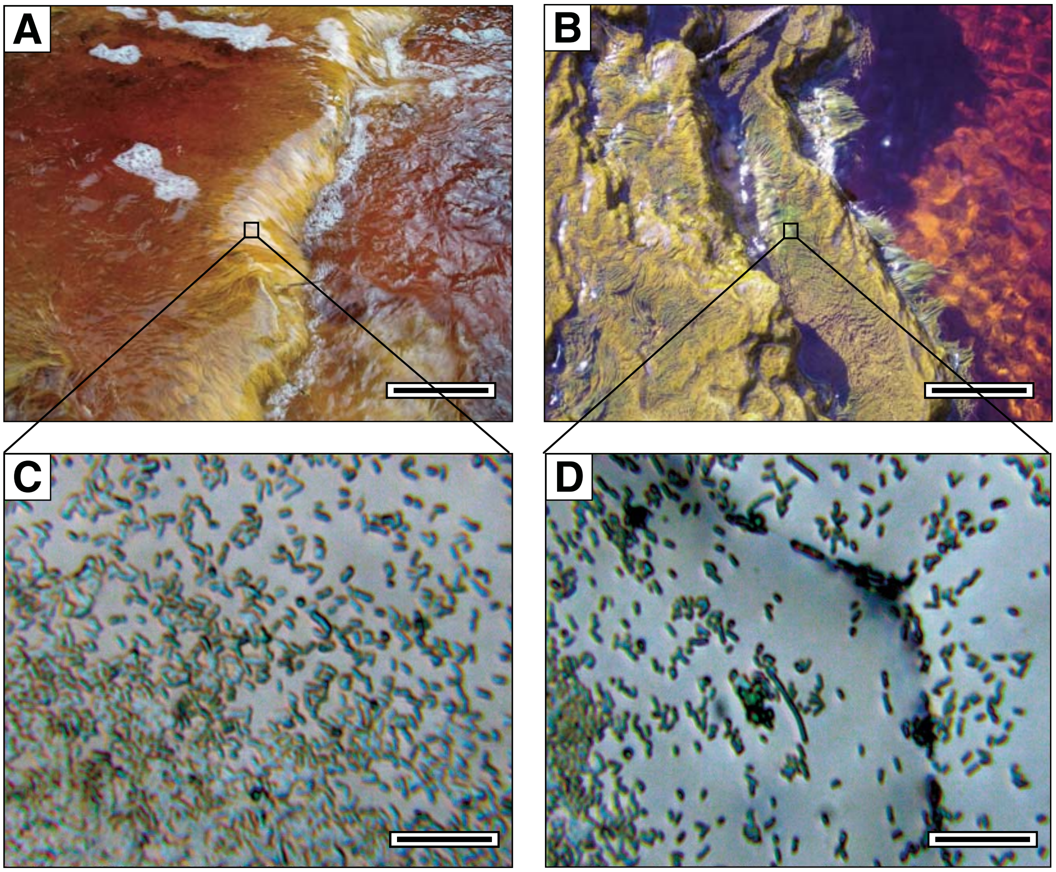

Figure 11. Field and microscopic aspect of the white bacterial streamers that have colonized the stream substrate between T-2 and T-5 (TIF section). (A–B) Field aspect (the scale bar represents 40 cm in A and ~5 cm in B). (C–D) Bacterial cell suspensions taken from A–B (under transmitted light petrographic microscope; scale bars are 3 μm). TIF—terraced iron formation.

Leptothrix) alternating with sand deposition and erosive episodes.

From Brake and co-workers, the water chemistry of the acidic effluents clearly determines the density and distribution of the microbial communities. Thus, in their 2001 paper, Brake et al. suggested that *Euglena mutabilis* tolerates very acidic conditions (pH 1.7–4.6) and high metal contents (e.g., up to 12,110 mg/L Fe, or 1840 mg/L Al), although extremely high concentrations of sulfate (on the order of tens of grams per liter) may have an adverse effect on this acidophilic protozoan. Also, these authors reported that the cool water temperatures that take place during the winter, as well as extremely high concentrations of dissolved solids (i.e., sulfate and metals), strongly limit the presence of diatoms in the acidic effluents at Green Valley (Brake et al., 2004).

The concentration of sulfate and the major cations present in the Tintillo acidic river are moderately constant all year round, although significant differences may exist in the content of some potentially toxic trace elements such as As, Cd, Co, Cr, and U (Table 1). However, the reported diatoms and euglenophytes in the pre-TIF section appear to tolerate very high sulfate and metal concentrations during most of the year, so that the water chemistry does not seem to control their distribution to a great extent. Rather, the factor that most critically determines the presence or absence of these photosynthetic microbes in the Tintillo River seems to be the amount of solar light penetrating into the water column, which in turn depends on the concentration of Fe(III) (both dissolved and particulate) in the stream water. The presence of large amounts of Fe(III) colloids (Fig. 12C) provokes a sharp transparency decrease, and the photosynthetic activity of diatoms and euglenophytes becomes deeply limited. This seems to be the principal reason by which these microorganisms are present in the section between the source area and the beginning of the iron terraces, while no sign of diatoms or euglenophytes is observed in the TIF section in association with the iron precipitates. Therefore, these microbes would not act as "active builders" of the Fe-rich terraces, although they indirectly favor (along with the green algae) the formation of iron terraces by increasing the content of dissolved O_2 available in the system (via photosynthesis), which in turn enhances the metabolic activity of the Fe(II)-oxidizing bacteria.

The case of the TIFs in the Tintillo River seems to be closer to the Fe-rich stromatolites of the Carnoulés Pb-Zn mine in Gard, France, in that they seem to be intimately associated with the presence, distribution, and metabolic activity of the bacterial mats that cover the submerged and presently forming iron terraces. Some of the internal macro- and microtextures recognized in the field and under the microscope (mound-shaped structures, fiber-shaped growths) resemble organically derived structures and suggest that the Fe-oxidizing bacteria are playing a critical role in the formation of these macrostructures, not only as "passive oxidizers" of Fe(II), but also as "active builders" of the ocherous solid material. The alternation of wavy and sponge-like laminae, as well as the fibrous growths (Figs. 5–7), seems to depict relics of bacterial streamers. In this sense, these iron deposits could be satisfactorily considered as organosedimentary structures formed by the successive alternation of biologically derived laminae and inorganically precipitated Fe(III)-rich layers. This lamination is considered to record hydrological cycles with different rates of bacterial growth and schwertmanite precipitation. Thus, the dry/summer periods under low-flow conditions and warmer temperatures would favor the development of thick biofilms containing dense bacterial communities capable of forming thin biolaminates by the oxidation of Fe(II) and the precipitation of Fe(III).

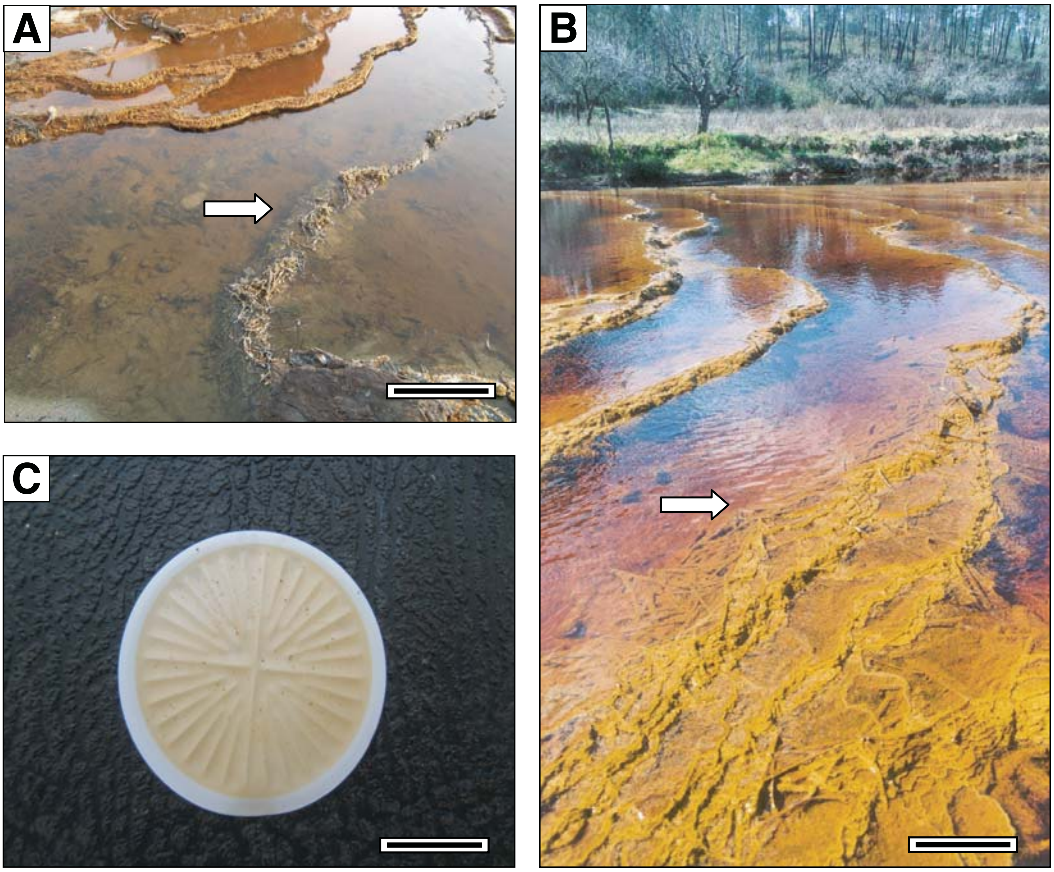

Figure 12. Field evidence of inorganic mineral precipitation. (A–B) The white arrows point toward terraces formed by the accumulation of fallen pine leaves and the subsequent cementation by efflorescent sulfate salts (halotrichite, copiapite; A) and/or hydrous iron oxyhydroxides (schwertmannite; B); the scale bar is around 40 cm in length in both cases. (C) Detail of a 0.45 µm membrane filter used during filtration of water at the sampling site shown in B (scale bar is around 1 cm in length).

This biogenic accumulation of Fe(III) would take place either by direct absorption (e.g., by extracellular assimilation, or by entrapment of Fe[III] colloids in the bacterial mucilage) or by inorganic precipitation preferentially occurring above the biofilms (which would act as nucleation sites; Leblanc et al., 1996; Kawano and Tomita, 2001; Ehrlich, 2002; Jones and Renaut, 2007). On the other hand, the higher-flow conditions and cooler temperatures that take place during the winter could temporarily remove part of the benthic microbial communities and increase the pH, thus favoring mineral precipitation and the formation of thick, massive layers composed of aggregated spherulites of schwertmanite, which would be subsequently recrystallized and transformed into more stable goethite after a few months or years. The consecutive alternation of these different episodes could perfectly explain the present-day morphology and microtextures of the terraced iron formations.

Travertine-Forming Springs and Subtidal Stromatolites in Calcareous Environments: The Inorganic Perspective

The sedimentary features and internal structure displayed by the TIFs of the Tintillo River are morphologically similar to those described in many calcareous travertines deposited in karstic systems (e.g., Golubic, 1973; Pentecost, 1978; Pentecost and Spiro, 1990) and in hydrothermal hot springs (e.g., Renaut and Jones, 1997; Jones and Renaut, 1998; Renaut et al., 1998; Fouke et al., 2000; Van Gundy, 2003). These formations have been the subject of considerable scientific attention by researchers from a variety of fields including classical disciplines like sedimentology and mineralogy, and more recently, aqueous geochemistry, physics, or mathematics. For example, Golubic (1973) stated that the outward growth of cyanobacteria, to avoid being trapped by the carbonate sediment, contributes to the porosity of travertines formed in freshwater courses, whereas Pentecost (1978) and Pentecost and Spiro (1990) estimated that the contribution of these microbes to the calcification process in travertine formation may amount to no more than ~10%, and the rest of the $CaCO_3$ is formed abiotically as a result of degassing (loss of CO_2) of stream water. More recently, Renaut and Jones (1997, 2000), Jones and Renaut (1998), and Renaut et al. (1998) have studied the role of microbes in the formation of travertine and siliceous sinter in hot and boiling springs in the Kenya Rift Valley. These authors proposed, based on petrographic and mineralogical evidences, a purely inorganic origin for the carbonate travertines deposited in the hot springs of this area, whereas, on the other hand, they defend a microbial origin for the siliceous sinter deposits studied in the same region. Also, Fouke et al. (2000) and Van Gundy (2003) have studied the relationships between the microbial life present in the Mammoth travertine-depositing hot springs at Yellowstone National Park and the geomorphology of these spring systems. Van Gundy (2003) has created an artificial hot spring within the laboratory to investigate the possibility of creating formations similar to those in nature without the microbial life. Preliminary research indicates that such formations may be independent, not only of microbes, but of crystalline structure and water chemistry, as well. Finally, Hammer et al. (2005a, 2005b) have developed a computer model that successfully simulates and explains the typical geological pattern displayed by the travertine terraces in calcium-carbonate spring systems. This model, which did not include elements like reaction, transport, and degassing of chemical species, carbonate precipitation, or surface tension, involves a coupling between the precipitation rate and hydrodynamics (based on shallow water flow and a correlation between the flow velocity and precipitation), with microbial activity playing a minor role.

In addition to the calcareous travertines deposited by Ca-HCO_3–rich groundwaters and hot springs, a comparison between the iron terraces of the Tintillo River and the calcareous stromatolites formed in marine (shore) environments seems pertinent. Interpretations of these typical sedimentary structures have evolved considerably, from the mainly organic (bacterial) nature, which sedimentologists attributed to these formations in the 1970s (e.g., Awramik et al., 1976; Golubic, 1976; Walter, 1976, 1994), to more recent abiotic theories based on current research using physical and numerical computer modeling (e.g., Grotzinger and Rothman, 1996; Grotzinger and Knoll, 1999; Batchelor et al., 2000). Grotzinger and colleagues have successfully modeled a growth pattern similar to those of stromatolites based upon diffusion-limited aggregation and sedimentation of either microbial mats or precipitated minerals.

Organic and Inorganic Processes Proposed for the Development of TIFs

Inorganic Processes

In agreement with the cited research on the calcareous travertine systems, strong field and geochemical evidence exists to support an inorganic origin for some of the studied terraces in the Tintillo River. Field evidence includes (1) young, incipient terraces of 10 m to 15 m in length that have formed over a sedimentary substratum composed of fallen pine leaves and that do not have any sign of underlying or overlying bacterial mats (Figs. 12A–12B), and (2) smaller, 0.5–1-m-long terraces that have formed by coalescing, small rims nucleated around pebbles. From a geochemical perspective, the Tintillo acidic water has been found to be strongly oversaturated with respect to schwertmanite, jarosite, and goethite (Sánchez-España et al., 2005a, 2005c), so that any small, pre-existing obstacle, barrier, or solid may easily provoke the nucleation and further precipitation of Fe(III) minerals in the stream water and above the substrate. In fact, significant amounts of Fe(III) particles are usually observed during filtration of water through 0.45 μm and 0.1 μm membrane filters (Fig. 12C). Moreover, it is often possible to recognize a bimodal character of these solid particles retained by the filter, with very fine-grained, light orange to yellow colloids, which probably consist of nanocrystalline schwertmanite, covering most of the filter, and other, coarser, dark orange to brownish particles (probably goethite) randomly dispersed on the filter surface.

This set of observations allows us to conclude that purely inorganic, physico-chemical processes can also account for the formation of TIFs. Thus, incipient rims formed by fallen pine leaves or stream cobble would induce the precipitation of schwertmanite (±goethite ± jarosite) along and around these barriers and a subsequent migration of the iron deposit upward and downward in a similar manner to that proposed for the development of calcareous travertines. The hydrous iron oxides tend to be quickly dehydrated and recrystallized into more stable forms (schwertmanite and/or jarosite are converted to goethite), which allows the physical stabilization of the prototerraces, and constitutes a good substrate either for (1) further mineral growth, (2) colonization of bacterial biofilms, or (3) further accumulation of detritic material (leaves, sand, cobble, etc.), with subsequent cementation by newly nucleated and precipitated iron oxides.

During the high-flow conditions typical of the winter months, rainfall episodes can enhance the rate of mineral precipitation by either (1) pH increase, or (2) oxygenation enhancing oxidation and precipitation of dissolved iron, and (3) higher flow velocity, which increases precipitation rate. Conversely, the dry and low-flow conditions that prevail in summer favor evaporation and slight decreases of pH, as well as lower stream-flow velocities, thus decreasing the precipitation rate. Hence, the internal lamination observed in the iron terraces would be recording hydrological cycles.

In spite of future experimental work to confirm these ideas, the morphological pattern displayed by the TIFs could be theoretically explained by the same linear equations used to model the calcareous travertines, which integrate flow velocity, surface topography, and precipitation rate (Hammer et al., 2005a). The coarsening of terrace edges (rims) and increase/decrease of the terrace frequency (wavelength) observed between different sites along the stream course may be due to an increase in the precipitation rate caused by changes in topography and water velocity. Similar TIF formations to those described in the Tintillo River have been observed in many other acid mine drainage systems of the Iberian Pyrite Belt (Fig. 13), including centimeter-scale terraces made of rozenite (Fe[II]-sulfate) in extremely acidic waters (pH < 1) in San Telmo mine, centimeter-scale terraces of schwertmanite-jarosite in Lomero mine, and meter-scale terraces made of schwertmanite in La Zarza mine (Sánchez-España et al., 2005a, 2005b, 2007). The internal arrangement displayed by all these formations appears to be identical in shape, which suggests that these deposits are fractal (not scale-dependent) in nature.

An evidence of the control that the inorganic factors have in the formation of TIFs arises from the observation that other acid mine drainage–impacted streams in the Iberian Pyrite Belt (such as the adjacent Tinto River) that have similar or higher iron concentration but notably lower pH values than those observed in the Tintillo show a significantly lesser development of these ocherous deposits. In these other cases, dense bacterial communities are also present in the stream channel (López-Archilla and Amils, 1999; López-Archilla et al., 2001; González-Toril et al., 2003; Fernández-Remolar et al., 2004), but the low pH of the water (below 2 in some instances) inhibits extensive inorganic precipitation of Fe(III), and although bacteria can effectively accumulate ferric iron on their cell surfaces (Kawano and Tomita, 2001; Ehrlich, 2002; Jones and Renaut, 2007), the hydrolysis rate is very low in comparison to that measured in the Tintillo.

Further, the formation of millimeter-scale microterraces composed of rozenite, a highly crystalline ferrous sulfate ($Fe^{II}SO_4{\cdot}4H_2O$), in an extremely acidic (pH < 0.5) and highly ferrous (>70 g/L Fe[II]) and anoxic acid mine drainage effluent in San Telmo mine (Fig. 13D; E. López-Pamo, 2006, personal commun.) strongly suggests that a microbially mediated oxidation is not critical for the formation of iron deposits with a travertine-like pattern. Although extremophile microorganisms have been detected in such extreme water (mainly acidophilic archaea like *Ferroplasma* and *Thermoplasma*; E. González-Toril, 2007, personal commun.), these microbes do not appear to have played a role in the nucleation and growth of these Fe(II) crystals, which would have precipitated from evaporative and highly concentrated waters under slow-flow to stagnant water.

Organic Processes

The presence of Fe(III) depends on the metabolic activity of the Fe-oxidizing bacteria, which are always present in variable proportions in most TIFs. However, a question arises about whether these microbes are merely passive elements in the formation of TIFs or if they contribute to the physical construction of these structures.

Whereas the inorganic processes can account for a good number of iron terraces studied in the Tintillo River (especially those in the T-1 to T-3 sections), other terraces located near T-3 and further downstream show abundant structures of probable organic origin, as previously described. The chemical sediments formed by precipitated ferric oxides in acid mine drainage–impacted rivers tend to be massive in texture, so that the highly porous, sponge-like, and filamentous structures recognized in the field

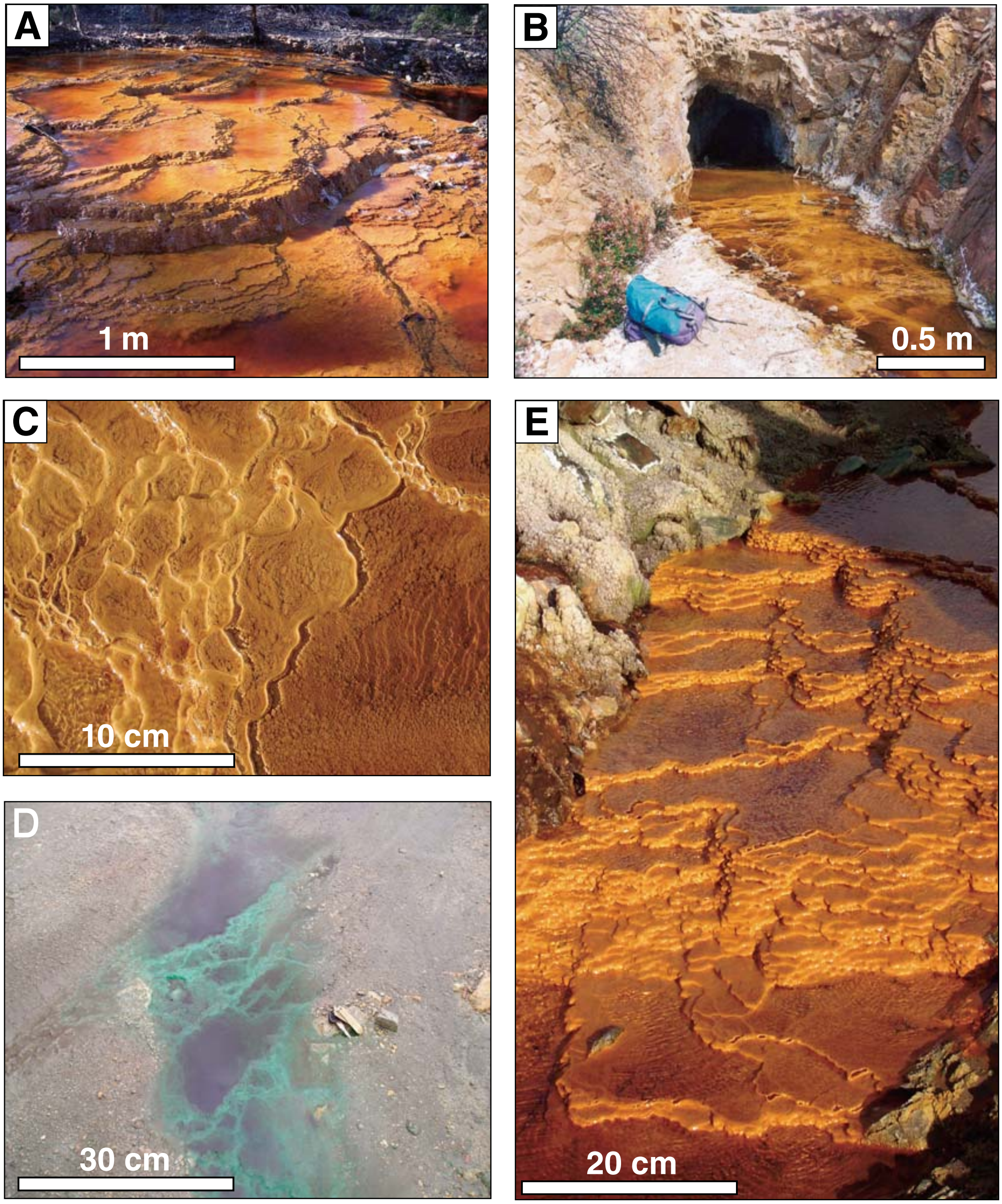

Figure 13. Examples of terraced iron formations (TIFs) of different scales in other mine drainage systems of the Iberian Pyrite Belt. (A) La Zarza (general aspect), (B) Lomero-Poyatos, (C) La Zarza (detail of small-scale terraces), (D) microterraces of millimetric scale made of rozenite ($Fe^{II}SO_4{\cdot}4H_2O$) in an acid mine drainage discharge from a waste pile in San Telmo mine, (E) schwertmanite terraces in an acid mine drainage emission in Tharsis mine (Filón Norte).

(Fig. 5) and under the microscope (Figs. 6–7) are considered to be compelling evidence for the active role of bacterial mats in the formation and/or coarsening of the iron terraces, as has been already proposed by other authors (Leblanc et al., 1996; Ehrlich, 2002). Such structures would thus represent fossil mats of Fe-oxidizing bacteria that were once buried by newly precipitated ferric oxides.

In addition to this lamination formed by the alternation of organic and inorganically formed layers, some other growth mechanisms directly or indirectly related to bacterial metabolism can be also proposed; for example, the thin schwertmanite layers are commonly observed floating on the water surface and have been interpreted as the result of nucleation and mineral growth around neustonic communities of Fe-oxidizing bacteria (Figs. 5E–5F). Once formed, and when a critical thickness is reached, these layers tend to sink and settle on the bottom of pools, thus contributing to the solid structure of the terraces. Also, the mound-shaped structures (Figs. 5A–5B) could be tentatively explained as bacterial colonies. These small mounds tend to coalesce and form incipient rims and prototerraces, which can grow by further bacterial colonization and/or mineral precipitation.

On the other hand, and unlike other similar formations studied in comparable acid mine drainage systems (e.g., Indiana coal mines; Brake et al., 2001, 2002), the photosynthetic eukaryotes (green algae, euglenophytes, diatoms) do not seem to play a relevant role in the formation of TIFs in the studied area. They are, however, secondary actors providing important amounts of dissolved oxygen (through photosynthesis) and carbon (through fixation of CO_2 and decomposition) for the Fe-oxidizing bacteria.

Environmental Significance

TIFs have an important environmental significance in their capacity to scavenge some metals from the stream water. This metal retention is especially important for iron, although the retention of some toxic trace elements such as Cu, As, and Pb is also significant. The iron concentration of the TIFs is around 60 wt% Fe_2O_3 (equivalent to around 420,000 ppm Fe) on average (Table 2), which represents a concentration factor of around 233 with respect to the aqueous content (~1800 ppm; Table 1). This accumulation of iron in the solid phase along the stream channel is especially evident in the section between T-4 and T-5, where the precipitation of iron implies the loss of between 14% (June 2003) and 18% (March 2004) of the iron loading (Table 1). All together, this removal of iron represents a loss of iron mass flow of around 11 mg/s in June 2003 and 32 mg/s in March 2004. On average, these quantities represent the removal of between 460 and 1000 tons of metallic iron per year. Considering the length and average width of the cited stream sections, such iron removal would represent, assuming that all the iron is precipitated on the streambed, an accumulation solid ferric iron of between 1 and 2 cm/yr. This growth rate is low if compared, for example, with measured growth rates in the Mammoth Hot Springs at Yellow National Park, USA (~30 cm/yr; Fouke et al., 2000). However, the value of 1 cm/yr matches with the thickness of some terraces (up to 1 m) and the estimated age of the acid mine drainage processes in the current channel of the Tintillo River (around 100 yr).

In addition to the removal of iron through direct precipitation, some trace elements, such as As and Pb, also appear to be significantly retained in the TIFs by sorption processes. Although the concentrations of these elements in the TIFs are not extraordinarily high (average contents of 963 and 334 ppm for As and Pb, respectively), if they are compared with their corresponding average aqueous concentrations (around 260×10^{-3} and 28×10^{-3} ppm, respectively), extremely high concentration factors of 3700 and 11,930 are obtained, respectively. Therefore, these two highly toxic elements are significantly scavenged and retained in the TIFs; this represents an environmental benefit. Conversely, other more soluble metals, such as Mn, Cu, and Zn, do not seem to be significantly affected by this scavenging process (concentration factors for these three metals are 2.6, 4.5, and 0.7, respectively).

CONCLUDING REMARKS

In this work, we have presented a number of geochemical, mineralogical, morphological, and microbiological observations from a unique system of terraced iron formations that is presently being formed in the Tintillo acidic river. These spectacular formations are the result of the interaction between (1) highly acidic and Fe(II)-enriched waters, (2) atmospheric oxygen, and (3) acidophilic microbes that have found perfect habitats for their Fe-oxidizing metabolisms in these extreme environments. For the moment, there is no definitive evidence to conclude whether the terraced iron formations of the Tintillo River and those observed in many other acid mine drainage systems worldwide are purely organic or inorganic in origin, although in the authors' opinion, the most probable hypothesis is a combination of both types of processes interplaying at the same time. The abiotic processes could be more important than the biotic factors in winter (higher flow, lower temperature), and conversely, the bacterial activity could play a major role in summer (lower flow, higher temperature).

TIFs formed in acidic mine drainage environments are unique geomicrobiological systems that can provide highly relevant information about the interaction between extremophile acidophilic microbes and their surrounding aqueous environments, as well as about the ability of microbes to modify environmental factors such as water composition or geometry of water courses. Moreover, TIFs represent interesting associations of iron and microbes, which could be useful models with which to compare the Fe-oxide deposits recently observed on Mars. Further research on the TIFs of the Tintillo River and others with similar characteristics should include well-designed laboratory experiments in order to simulate the formation of TIFs under controlled conditions and identify the precise role played by microbes in the formation of such deposits. The application of computer-assisted numerical modeling and a multidisciplinary perspective in which hydrogeochemists, microbiologists, and sedimentologists can interact and work together would strongly improve our understanding of the processes involved in the formation of TIFs.

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