INTRODUCTION

The massive sulfide deposits of southern Spain and Portugal were formed about 300 Ma by precipitation from hydrothermal fluids during a period of intense submarine volcanism (Boulter, 1993). Subsequent uplift and compression resulted in the distribution of >1000 Mt (million metric tons) of massive sulfide ore bodies over a region 250 km long and 30 km wide, known today as the Iberian pyrite belt (Munha et al., 1986; Fig. 1). The deposits typically contain 50% sulfur, 42% iron, 2%–8% copper + lead + zinc by weight and significant quantities of gold and silver (Strauss et al., 1977). Early indications of mining in the region date to the third millennium B.C. Silver deposits later became an important source of wealth for the Phoenicians (Morral, 1990). About 5 Mt of pyrite had been mined from the Rio Tinto by the time Carthage fell at the end of the Third Punic War in 146 B.C. (Pinedo, 1963). Spain became a Roman province, and mining of the rich deposits of the Iberian pyrite belt for copper and silver started on a larger scale. Still-visible slag deposits indicate that about 25 Mt of sulfide ore was mined from the region by the Romans through the 4th century A.D. (Strauss et al., 1977). The sites then remained virtually untouched until the mid-19th century when mining started again, initially driven by the demand for copper and later also for sulfuric acid.
About 250 Mt of sulfide ore were extracted from the Iberian pyrite belt from the mid-19th century through the late 1970s, about one-half of the total from a single deposit, the Rio Tinto, and another third from the nearby La Zarza and Tharsis mines (Strauss et al., 1977; Fig. 1). Until the 1970s when a number of new sites came under produc-

tion, most of the mining activity in the Iberian pyrite belt was restricted to the relatively small watershed of the Tinto and Odie1 rivers.

**METAL ENRICHMENTS IN RIVER AND SEA WATER**

It has been known for some time that Spanish coastal waters of the Gulf of Cadiz are highly enriched in a number of metals including Cd, Cu, and Zn and that these enrichments are advected to the western Mediterranean through the Strait of Gibraltar (Boyle et al., 1985; Sherrell and Boyle, 1988; van Geen et al., 1988; 1990; 1991; van Geen and Boyle, 1990). Some of these observations are summarized in Figure 1 which shows the distribution of dissolved Zn in surface waters of the region. The range of Zn concentrations observed in 1986 and 1988 extends from <1 x 10^{-9} mol/kg in surface Atlantic waters unaffected by Spanish shelf water to as high as 200 x 10^{-9} mol/kg south of the mouth of the Guadalquivir River. Patterns of Cd and Cu enrichments throughout the region closely parallel the Zn pattern (Fig. 2). Metal concentrations in the two main rivers of the region, the Guadiana (watershed of 68 000 km², mean discharge 80 m³/s) and the Guadalquivir (57 000 km², 160 m³/s), however, are comparable to rivers draining other industrialized regions and cannot explain the observed levels of enrichment. Prompted by reports of metal contamination in the Tinto-Odiel rivers and estuary (Garcia-Vargas et al., 1980; Nelson and Lamotte, 1993), we sampled the waters of this relatively small system (combined watershed 3400 km², mean discharge 20 m³/s, J. Borrego, 1996, personal commun.). Concentrations of Cd, Cu, and Zn in filtered samples collected from the Tinto river in December 1992 were >1000-fold higher than in either the Guadiana or the Guadalquivir rivers (Table 1).

Not all dissolved metals pass through the Tinto estuary with equal efficiency, however. Seawater proportions in samples collected within the estuary were determined from their Mg content. Relationships between the concentrations of Mg and other metals in December 1992 (not shown) indicate that although dissolved Cd mixes conservatively across the salinity gradient, there is significant removal of Cu and Zn from the water column onto suspended particles and/or bottom sediment. Since dissolved Cd passes the estuary without significant removal, it can be used as a reference to determine the relative proportion of different metals over the several orders of magnitude in concentration spanned by waters in the Gulf of Cadiz, the Strait of Gibraltar, and the western Mediterranean. Despite the different sampling years and run-off conditions, extrapolation of the shelf water data shows that the relationships between concentrations of Cd and other metals in surface waters throughout this region are dominated by input from a single source, the Tinto-Odiel estuary (Fig. 2). The data confirm that Ni is insufficiently enriched in the estuary to significantly affect the composition of surface waters of the Gulf of Cadiz. Leblanc et al. (1995) and Elbaz-Poulichet and Leblanc (1996) recently reached similar conclusions on the basis of dissolved metal concentrations measured in water from the Rio Tinto collected in July 1994.

The unusual features of Tinto River water can be attributed to mining of the sulfide ore in the watershed. Upstream from the Rio Tinto mine, the pH of the river is 7.2 (Garcia-Vargas et al., 1980). The pH of the sample collected at Lucena del Puerto, 40 km upstream from the mouth, is 2.6; the

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**TABLE 1. COMPARISON OF SOURCE ORE AND RUN-OFF COMPOSITION IN TINTO-ODIEL WATERSHED**

<table>
<thead>
<tr>
<th>Element</th>
<th>Sulfide ore (µg/g)</th>
<th>Continental crust (µg/g)</th>
<th>Enrichment factor</th>
<th>Rio Tinto water (x10^{-9} mol/kg)</th>
<th>Mobilization relative to S</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>50000</td>
<td>260</td>
<td>1900</td>
<td>30000</td>
<td>1</td>
</tr>
<tr>
<td>Ag</td>
<td>18</td>
<td>0.07</td>
<td>240</td>
<td>&lt;0.0006</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Al</td>
<td>(30000)</td>
<td>160000</td>
<td>(0.2)</td>
<td>3200</td>
<td>(1.5)</td>
</tr>
<tr>
<td>As</td>
<td>4000</td>
<td>1.8</td>
<td>2200</td>
<td>2.2</td>
<td>0.46</td>
</tr>
<tr>
<td>Cd</td>
<td>(6.9)</td>
<td>0.2</td>
<td>(34)</td>
<td>2.0</td>
<td>(17)</td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
<td>25</td>
<td>4</td>
<td>19</td>
<td>4.6</td>
</tr>
<tr>
<td>Cu</td>
<td>6900</td>
<td>55</td>
<td>120</td>
<td>390</td>
<td>3.6</td>
</tr>
<tr>
<td>Fe</td>
<td>420000</td>
<td>72000</td>
<td>5.8</td>
<td>8800</td>
<td>0.61</td>
</tr>
<tr>
<td>Mn</td>
<td>400</td>
<td>1000</td>
<td>0.4</td>
<td>240</td>
<td>17</td>
</tr>
<tr>
<td>Ni</td>
<td>13</td>
<td>75</td>
<td>0.2</td>
<td>7.8</td>
<td>18</td>
</tr>
<tr>
<td>Pb</td>
<td>7600</td>
<td>12</td>
<td>630</td>
<td>0.43</td>
<td>0.006</td>
</tr>
<tr>
<td>Zn</td>
<td>13000</td>
<td>70</td>
<td>190</td>
<td>920</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Note: Co, Cu, Mn, Ni, Pb, and Zn data are mean for La Zarza ore (Strauss et al., 1981). Ag and As data show mean for Iberian pyrite belt (Strauss et al., 1977). Abundances in average continental crust from Taylor (1964).Rio Tinto dissolved-metal concentrations were determined by graphite furnace atomic absorption spectroscopy for Ag, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn. The sulfate concentration was determined by the method of Tabatabai (1974). As and Co data for Rio Tinto water are from Vatland (1996).

*All from Strauss et al., (1981) for rock sample #23 with high sulfide content.

*Cd from Murray Brook deposit of northeastern Canada similar in composition to Rio Tinto ore (Boyle, 1994).
decrease is due to sulfate oxidation. The riverine sulfate flux, calculated from a $30 \times 10^{-3}$ mol/kg concentration (Table 1) and the Tinto-Odiel River flow, corresponds to about 60% of the 1 Mt/yr mining rate of S in the Tinto-Odiel watershed over the past 100 yr (Strauss et al., 1977; Pinedo, 1963). Both Cu and Zn are enriched more than 100-fold in the ore relative to the mean composition of the Earth’s crust (Table 1). Because S is particularly enriched in the ore and mobile once oxidized, we can use it to index the relative mobility of other constituents in the ore. On the basis of a comparison of ore and river water composition normalized to sulfur, metals listed in Table 1 can be grouped into four categories: (1) Cd, Co, Cu, and Zn are enriched in the ore and possibly more mobile than S; (2) As, Fe, and S are enriched in the ore and of comparable mobility; (3) Ag and Pb are enriched in the ore but highly immobile; (4) Mn and Ni are somewhat depleted in the ore but enriched in the river. The last group suggests mobilization from other associated ores in the Iberian pyrite belt en- 

**HISTORY OF CONTAMINATION**

Mining activities in the Tinto-Odiel watershed have also affected the composition of estuarine and shelf sediments. Sediment enrichments attributable to mining do not span the same range as dissolved metal levels in the water column, but a plume of elevated Cu and Zn concentrations in surface sediments of the Gulf of Cadiz has been traced to its origin in the Tinto-Odiel estuary (Nelson and Lamothe, 1993; Palanques et al., 1995). Available data for metal enrichments in estuarine sediments as well as in acorn barnacles confirm that contamination of the nearby Guadi- 

**Figure 3. Downcore distributions of natural radionuclide $^{210}$Pb in disintegrations per min/g and metal Zn in sediment of cores TG25b (lat 37°00.8'N, long 7°11.7'W, 56 m depth) and TG22 (lat 36°53.0'N, long 6°54.1'W, 69 m depth) collected in 1986 from continental shelf south of Tinto-Odiel estuary. Horizontal dashed line indicates first departure of Zn concentration from background at 15.5 cm in both cores.**

Fine-grained particles in the water column are initially enriched in $^{210}$Pb relative to the radioactivity supported by their $^{238}$U content. As these particles accumulate over the shelf, excess $^{210}$Pb decays, and the resulting exponential activity profile with depth can be used to determine the sedimentation rate (Carpenter et al., 1984). In core TG25b, sediment mixing by benthic organisms down to 5 cm depth must also be taken into account. Figure 3 shows that the $^{210}$Pb data are consistent with sedimentation rates ranging from 0.08–0.12 cm/yr in core TG25b and 0.11–0.16 cm/yr in core TG22. Based on best fit model, ages of 15.5 cm horizon in cores TG25b and TG22 are 130 and 120 yr, respectively.

Although increased atmospheric Cu input during the peak of Roman activity in Spain has been detected as far away as Greenland (Hong et al., 1996), the impact on shelf sediments of the Gulf of Cadiz via the estuarine pathway during Roman times does not seem to have been comparable to that of mining over the past 120 yr. On the basis of a long-term mean sedimentation rate of ~0.07 cm/yr in the lower part of core TG25b, the inputs due to offshore dumping are equivalent to a small fraction of the river input to the Tinto-Odiel estuary (from Table 1, the mean discharge, and van Geen et al., 1991), it seems unlikely that offshore dumping could have created the surface water metal enrichment pattern of Figure 1.

The sediment contamination record allows us to evaluate the relative importance of the metal inputs to the Gulf of Cadiz. From 1977 to 1990, metal-rich acid effluents were transported daily from a titanium oxide processing plant operating in the Tinto-Odiel estuary and dumped near the center of the Gulf of Cadiz (van Geen et al., 1991; Nelson and Lamothe, 1993; Palanques et al., 1995). Because shelf sediments were contaminated well before dumping started and Cu and Zn...
age of the horizon at 223 cm can be estimated at ~3000 yr B.P. Because no significant Zn enrich-
ments were detected below 15.5 cm depth through-
out this core, we see no evidence of shelf sediment
contamination due to Roman mining.

CONCLUSIONS AND IMPLICATIONS

The effect of mining on the composition of the
Tinto river water is typical for sulfide ores. The
composition of a number of Welsh streams drain-
ing areas that have also been mined since Roman
times (Fuge et al., 1994), for instance, closely re-
sembles the river data in Table 1. To our knowl-
edge, the present study is the first recognition of a
metal signature originating mainly from one spe-
cific mining area that extends over several hun-
dred kilometres into the sea. Because run-off in
the region is highly variable seasonally and inter-
annually, the extent of the Tinto-Odiel dissolved
metal plume into the Gulf of Cadiz and the west-
ern Mediterranean is likely to vary as well (van
Geen et al., 1991).

Two cores show that metal concentrations in
shelf sediments increased during the second half
of the 19th century at the time of a rapid increase
in the scale of exploitation of the Rio Tinto mine. The
sediment cores also indicate that metal in-
puts from the Tinto-Odiel may have decreased signifi-
cantly over the past few decades, espe-
cially if the considerable lag expected from mixing
of sediment in the watershed and on the con-
tinental shelf is taken into account (Fig. 3). The
reduction may be due to the reduction in mining at
Río Tinto and improvement in ore extraction and treatment technology in other mines where
activities are concentrated today. The present
scale of contamination suggests that it will be dif-
cult to restore the Tinto-Odiel estuary to its con-
dition before mining on an industrial scale began.

It is not known to what extent metal contami-
nation of river water and sediment in the Tinto-
Odiel estuary over the past century has affected
the health of the local population. Inhabitants of
the area still consume shellfish from the estuary
as well as domestic animal products from the wa-
tershed. The state of the Tinto-Odiel estuary pre-

tains an opportunity to determine the impact of metal contamination by comparing the incidence of various illnesses in the area with that of in one of the nearby uncontaminated estuaries (Nelson and Lamothe, 1993).

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