

		ISSN 0016-7037 Volume 74, Number 15 August 1, 2010			
Geochimica et Cosmochimica Acta JOURNAL OF THE GEOCHEMICAL SOCIETY AND THE METEORITICAL SOCIETY					
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Mobility of iridium in terrestrial environments: Implications for the interpretation of impact-related mass-extinctions

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Received 2 October 2009; accepted in revised form 30 April 2010; available online 13 May 2010

Abstract

Traditionally, iridium has been considered an element of low mobility, but its behavior is still debated. Ir concentration in a soil affected by a catastrophic mining spill in 1998 that covered the soil with a layer of tailings offers the opportunity to analyse an exceptional Ir-bearing horizon 10 years after deposition. This has enabled comparisons with the values of past Ir-bearing horizons associated to impact-related mass-extinction events. Iridium concentration in the tailings (0.349 ppm) was 5-fold higher than the anomaly in the K–Pg at The Moody Creek Mine section (the highest values obtained from terrestrial sections). The oxidative weathering of the tailings caused the release of Ir and infiltration into the soil. Iridium distribution in depth indicates redistribution throughout the profile in relation to the change in the physico-chemical properties of the soil. With regard to the background concentration in the soil (0.056 ppm), anomalous values of Ir (0.129 ppm) can be detected to 11 cm below the layer of tailings. The correlation analysis between the Ir concentration and the main properties and constituents of the soils indicated a significant correlation with sulfur, iron, clay content, and pH. Selective extractions were made to study the forms in which Ir can be mobilized in the soil. The residual/insoluble fraction was >90% of the total Ir concentration in soil. Soluble-in-water concentration of Ir (1.5% of total) was detected in the uppermost 2–3 cm of the soil, which were directly affected by the leaching of acidic waters coming from the oxidation of the pyrite tailings. Iridium retention in the affected part of the soil reached 9% of the total Ir concentration; this retention could be related to the amorphous iron forms dissolved by the oxalic-oxalate extraction. However, according to our research, original Ir abundance could be secondarily modified, and then a direct analysis of the iridium values recorded in sediments could induce misinterpretations. The comparison between the actual example and the fossil record belonging to terrestrial settings, can be considered as a valuable approach, especially when Iridium data were used by researchers to interpret the impact-related mass-extinction events in the past.

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1. INTRODUCTION

Iridium is one of the platinum-group elements (PGE) together with Fe, Ni, and Co, considered as Group VIII transition metals. The PGE, along with rhenium and gold, are considered as highly siderophile elements, defined by their strong tendency to partition into metallic phases or to bond

with sulfur. This affinity results in very different properties during planetary differentiation compared to lithophile elements, reflected in their extraction from the mantle by core-forming metal and sulfides (Lorand et al., 2008). Therefore, iridium is relatively rare on Earth (natural background concentration in continental crust is 0.05 ppb; Wedepohl, 1995), and thus high concentrations of Ir have been associated with extraterrestrial origins. The most dominant species are Ir⁴⁺ and Ir³⁺, being the last usually found as soluble form. In seawater, the species of Ir are most likely to be oxy-hydroxyl and chloro-complex ion forms, although under oxidizing conditions shows a complicated chemical behavior, being the great importance the hydrolysis reactions for the sorption

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and desorption of this element in sediments (Dai et al., 2000). Anyway, the knowledge about the chemical speciation, mobility and sorption–desorption behavior of iridium is scarce.

Since the initial discovery of the Ir anomaly at the Cretaceous–Tertiary (K–Pg) boundary at Gubbio, Italy (Alvarez et al., 1980), probably the most characteristic feature, researches focused on the record of abnormal concentrations of Ir as revealing extraterrestrial source, mainly bolide impact, as its relationship with biotic extinctions, in both the marine and the terrestrial ecosystems. From the extreme case, reflected in the hypothesis of McLaren and Goodfellow (1990), proposing that all major extinctions might have been originated to extraterrestrial impacts, some of the different orders global bio-events occurring in the Phanerozoic (Walliser, 1996) have been interpreted as extraterrestrial in origin based on its association to iridium anomalies. Thus, aside from the K/Pg boundary mass-extinction event, consensually related to a bolide impact (from Alvarez et al., 1980), and recording all the associated impact evidences (i.e., spherules, Ir and other platinum-group anomalies, chromium isotope composition, and Ni-rich spinels, among others), including the occurrence of the Chicxulub crater at the Yucatan Peninsula (e.g., Hildebrand et al., 1991), others mass-extinctions have been associated with iridium anomalies and interpreted as consequence of giant impacts. Thus, along the Phanerozoic, and in order of decreasing age: the Precambrian/Cambrian boundary (Gostin et al., 1989), the latest Ordovician (Wang and Chai, 1989), the Frasnian/Famennian boundary at the Upper Devonian (Playford et al., 1984; McLaren, 1985; Geldsetzer et al., 1987; Goodfellow et al., 1988; Wang et al., 1991, 1996), the Permian/Triassic boundary (Xu et al., 1985; Xu and Yan, 1993), the Triassic/Jurassic boundary (Olsen et al., 2002, 2003), and the Late Eocene (Keller et al., 1987).

However, even the association between mass-extinction events other than the K–Pg and high concentrations in extraterrestrial Ir has been largely interpreted, this is not unequivocal, and for some researchers sole Ir anomalies, with the absence of other typical features evidencing extraterrestrial origin, are not sufficient to support meteorite impacts. Iridium concentrations concurrent with major and minor extinction events have been related to diverse genesis other than the extraterrestrial origin. In example, changes in paleo-redox conditions during deposition and/or early diagenesis, variations in sedimentation rates, terrestrial enrichment, volcanic eruptions, or local biological processes, among others, have been also proposed to explain Ir concentrations associated to mass-extinction as those from: the latest Ordovician (Wang et al., 1992), and the Ordovician/Silurian boundary (Orth et al., 1986; Wilde et al., 1986), the Frasnian/Famennian boundary at the Upper Devonian (McLaren, 1985; Hurley and Van der Voo, 1990; Wallace et al., 1991; Wang et al., 1991), the Devonian/Carboniferous boundary (Wang et al., 1993), the Lower Mississippian at the Lower Carboniferous (Orth et al., 1988a), the Permian/Triassic boundary (Chifang et al., 1992; Retallack et al., 1998), the Triassic/Jurassic boundary (Kerr, 2002), the Late Cenomanian (Orth et al., 1988b, 1993), and the latest Paleocene (Schmitz et al.,

1997). Even so, in most of these cases the extraterrestrial impact was also considered and not definitively precluded (i.e., Orth et al., 1988a,b, 1993; Wang et al., 1991, 1992; Chifang et al., 1992; Schmitz et al., 1997).

The variable, and even curious debate, involving iridium anomalies, mass-extinctions, and impact events can be illustrate in two particular cases: (a) the Permian/Triassic boundary, where significant iridium anomalies from samples reported from outcrops in China, were not registered from the same samples analyzed in other laboratories (Zhou and Kyte, 1988; Yang et al., 1993; Braun et al., 2001; Farley and Mukhopadhyay, 2001; Koeberl et al., 2002, and references in Holser et al. (1989)), and (b) the Late Eocene (Eocene–Oligocene transition), with iridium anomalies related by some researchers to impact events (Montanari, 1988; Montanari et al., 1993; Kyte and Liu, 2002), were not associated to extinctions, but only with major assemblage changes (Keller et al., 1987; Coccioni et al., 2002), precluding the interpretation of an extraterrestrial impact for other authors (Monechi et al., 2000), even the extraterrestrial body impact was confirmed by the earth cratering record (Montanari et al., 1998).

As above indicated, from all the registered Phanerozoic bio-events, the K/Pg mass-extinction event, involving the marine and the terrestrial ecosystems, is unequivocally related to an extraterrestrial bolide impact, showing generalized and significant iridium anomalies at the K/Pg boundary layer, as well as other impact features (Smit, 1999), determining that can be considered as the most valuable example to study. Database on the K/Pg boundary show that Ir anomaly has been spread homogeneously all around the globe, in different depositional environments, from deep marine to continental settings (Claeys et al., 2002). In terrestrials sections, iridium concentrations at the K/Pg boundary layer are lower than in marine ones, but with values significantly enriched respect to the average background (Orth et al., 1981; Nichols et al., 1986; Lerbekmo et al., 1987; Pillmore et al., 1999; Vадja et al., 2001; Hartman et al., 2002).

Iridium data (i.e., maximum iridium concentration, integrated iridium concentration in the boundary clay or Ir fluxes; nanograms per square centimeter, Os/Ir, Ru/Ir and Pt/Ir ratios) at the different K/Pg boundary sites has been used to interpret impact features as the size of the bolide, nature of the K–Pg impactor, or the distance from the impact (Alvarez et al., 1980; Kyte and Wasson, 1982; Roddy et al., 1991; Sigurdsson et al., 1992; Vickery et al., 1992; Donaldson and Hildebrand, 2001; Frey and Frey, 2002; Paquay et al., 2008). Abundance of iridium in the K–Pg ejecta layer (the boundary layer) depend on several factors as the distance from the Chicxulub crater, the depositional setting, and the preservation of the K–Pg boundary layer. In terms of distance from the crater, and according the features of the ejecta layer at the K/Pg boundary, Smit (1999) differentiated between: (a) proximal sites, mainly occurring in the Gulf of Mexico, the Caribbean, and the east coast of the United States up to New Jersey and DSDP Site 603, at <2500 km from the crater, with a thick >3-cm layer, and iridium concentrations sometimes indicating remobilization of the ejecta layer (see figure 10 in Smit (1999) for iridium

profiles of the proximal sites), (b) intermediate sites, 2000–4000 km from the Chicxulub crater, corresponding to continental North America sites, with the thickness of the ejecta layer between 0.5 and 2 cm, and (c) the distal sites, more than 7000 km from the Chicxulub crater, with a ejecta layer only a few millimeters-thick (2–3 mm), including some of the most complete, expanded and well exposed K/Pg boundary sections in the world as the Caravaca section (Smit, 1990, 2005). Iridium data base reveals that Ir concentration is diluted at proximal sites due to the high volume of sediment put in suspension in the Gulf of Mexico after the impact (Claeys et al., 2002). According the depositional setting, in shallow-water sequences is not rare to found the K/Pg boundary as a gap due to the existence of interruptions in sedimentation (i.e., diastems, discontinuities, disconformities), that is not obvious in deep-water sequences, except in the most deep-sea records due to the extremely low sedimentation rates, deepening of the calcium carbonate compensation, slumping and contour or turbidity currents (Smit, 1999).

At the K–Pg boundary event, occasionally variations in the concentration of Ir across the K–Pg boundary transition, above and below the event horizon, have been recognized and related with diverse phenomena (Evans and Chai, 1997; Claeys et al., 2002). Remobilization of Ir during high and/or low temperature conditions has been interpreted as consequence of: (a) existence of a reducing environment at the time of deposition, together with the distribution in the sediment column after bioturbation (Officer and Drake, 1983; Pospichal et al., 1990), (b) microbial activity (Schmitz et al., 1988; Dyer et al., 1989), (c) suboxic conditions (De Lange et al., 1991), (d) postdepositional processes, including diffusion (Robin et al., 1991; Lee et al., 2003), (e) sedimentary redox changes (Colodner et al., 1992), (f) mobility of Ir in the lithified sediments and residence time of this element (Ben Abdelkader et al., 1997), and (g) diagenetic alteration of the ejecta layer (Martínez-Ruiz et al., 1999).

However, in spite of the significance of Ir in the context of the mass-extinction events, related or not with an extraterrestrial origin, behavior of Ir during depositional and postdepositional conditions is not well established, that introduce significant uncertainty regarding variations of the original Ir concentrations. Iridium is considered one of the less mobile of the PGE elements and is low distributed in sedimentary environments (Colodner et al., 1992; Evans et al., 1993). There are evidences of postdepositional mobilization after changes in sedimentary conditions (Izett, 1990; Wallace et al., 1990; Evans et al., 1995), but little is known about Ir mobility in terrestrial environments. The lower mobility of Ir in relation to the other elements in soils would produce its selective concentration in relation to the bedrock, by the action of the soil forming factors over time. Concentrations of Ir up to 45 ppb has been described in sediments in American lakes (Crompton, 2001), indicating an enrichment 900 times higher than the values in continental crust, and 5 times higher than concentration in K–Pg boundary at Gubbio, Italy (Alvarez et al., 1980).

According the above commented significance of the iridium anomaly for the interpretation of the impact-related mass-extinctions, with special significance in the K/Pg

boundary event (being probably the most characteristic feature), to approach the behavior of iridium into the sediments, and then any possible postdepositional variation of the iridium values, reveals of major interest. Iridium data used to characterize impact features can correspond not to original values but to secondarily altered ones, that could determine misinterpretations. This could be the case if the mobility of the iridium is proved. The disaster of Aznalcóllar (the failure of a tailing pond at the pyrite mine of Aznalcóllar, province of Seville, 25 April 1998), offers us the possibility to working on soils intensively polluted, including a high concentration of iridium. The aim of this paper is to evidence the mobility of Ir in continental polluted sediments after physico-chemical changes in sedimentary conditions, and its translocation in depth into the soil profile. The obtained results reveal of great interest for the analysis of Ir-bearing horizons, preventing on a direct interpretation of the registered Ir values in the fossil record, and showing significant implications, especially in those cases corresponding to impact-related mass-extinction events.

2. MATERIALS AND METHODS

The study area (Fig. 1), located in Sevilla (SW Spain), was affected by a spill from a pyrite mine in 1998 (disaster of Aznalcóllar). The tailings spilled were the waste deposit from the extractive procedure of the main ores (Zn, Pb, Cu, and As) contained in form of sulfides. The mineral extraction produced the selective concentration of Ir and heavy metals in the tailings; this ore-processing residue had a mineral composition dominated by pyrite (85–90%) with minor amounts of other polymetallic sulfides which were stored in a pond under reductive conditions mixed with acidic waters. After the accident, the affected soils located on the fluvial plain of the Guadamar River were covered by a layer of slurry from the spill. Remediation measures involved the clean-up of the soils, but in some parts, experimental plots (50 × 30 m) were preserved with the tailings for research purposes (Martín et al., 2008). The present study was performed in one of these plots, where a thin layer of tailings (2–5 cm) covered the soil for 10 years. The recovery of biological activity in these plots was previously studied and comparisons were made with data from the K–Pg mass-extinction (Rodríguez-Tovar and Martín-Peinado, 2009).

In 1998 the layer of tailing that covered the soil registered anomalous concentration of Ir, reaching 0.349 ppm (Table 1) due to the selective extraction procedure of exploitable elements. This concentration was 38.8-fold higher than the anomaly in the K–Pg boundary layer at Gubbio (first discovery of the Ir anomaly at the K–Pg boundary), 9.9-fold higher than the anomaly at Caravaca (one of the most complete K–Pg boundary sections), 5-fold higher than the anomaly in The Moody Creek Mine section (the highest values obtained from terrestrial sections) and 6.2-fold higher than the background concentration of the study area (see Rodríguez-Tovar and Martín-Peinado, 2009 for a compilation of Ir values in the K–Pg boundary layer of significant sections).

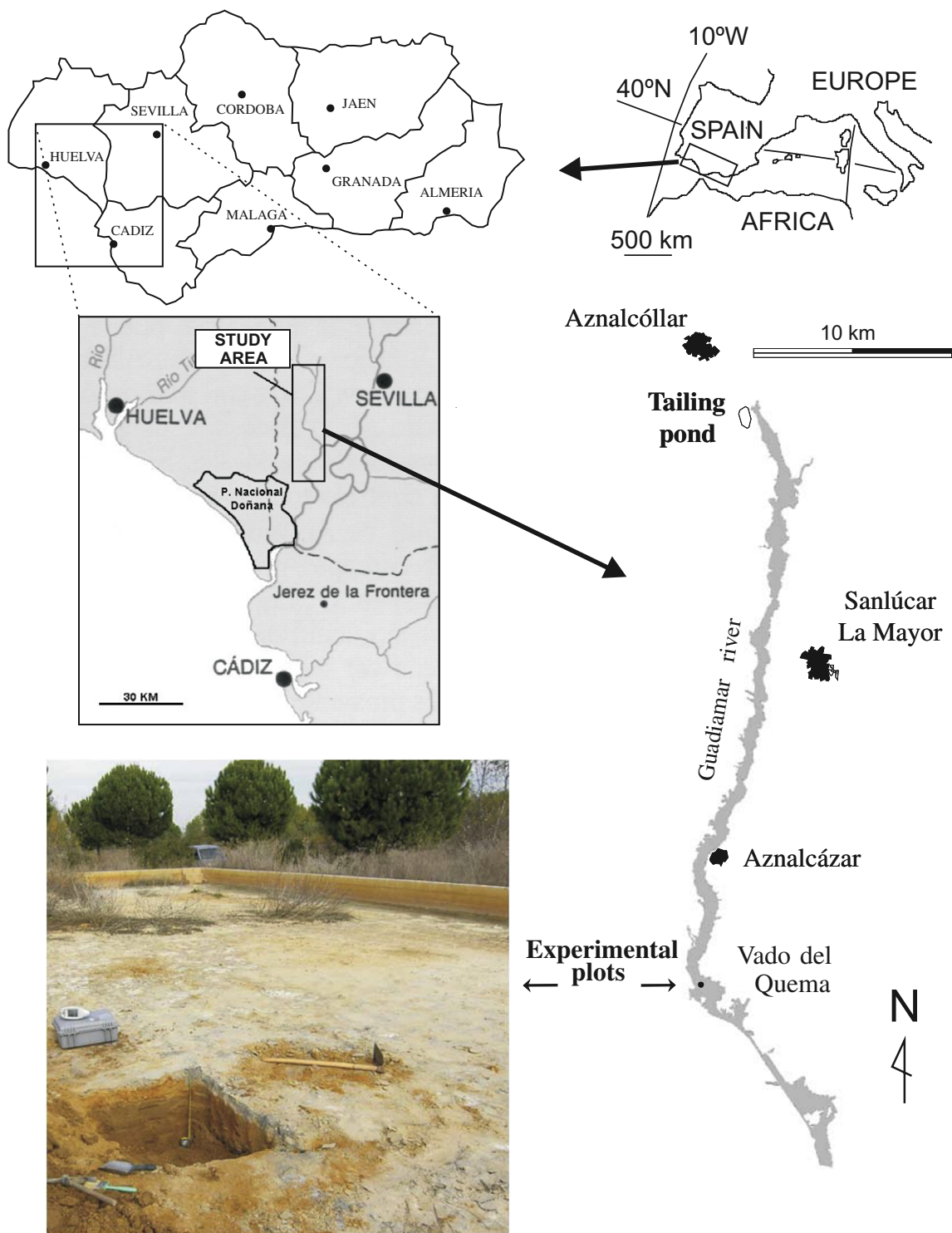


Fig. 1. Location of the study area (Vado del Quema) at the province of Sevilla (SW Spain), close to the Parque Nacional de Doñana, and precise position of the experimental plots (including photograph) at the Guadamar river. Note that grey color in the Guadamar river corresponds to the flooding plane of the river affected by the tailing spill.

Just after the accident, the tailings deposited over the soil remained saturated in water and the local conditions were anoxic, the presence of pyrite and acidic-sulfate waters could be important similarities with the original geo-

chemical situation of Ir in the sedimentary environment (Premovic et al., 2006).

A few weeks after the deposition, as a consequence of the drying and aeration of the media, the tailing began to

Table 1

Concentration of Ir and other elements (in ppm) in the pyrite tailings and in the uppermost 10 cm of the soils, in the year of the mining spill (1998) and 10 years later (2008).

	Ir	Zn	Cu	Pb	As
Tailing98	0.349	6922.6	2009.1	9507.3	3859.6
Tailing08	0.139	1415.1	333.3	12721.2	2803.2
Soil98	0.056	144.6	33.8	64.6	29.0
Soil08	0.129	240.6	173.5	1793.7	1302.3

oxidize, resulting in a marked change of the physico-chemical properties of the original soil. The main transformations involved strong acidification (soil pH decreased from 7.6 to 2.4), an intense release of sulfate salts and heavy metals, and a pronounced change in the color of the soil in depth (Simón et al., 2001; Dorronsoro et al., 2002). In our case, the unaffected soil had a dark-brown color from 42 cm in depth. The background concentration of Ir in the soil was very high (0.056 ppm; Table 1), being 6.2- and 1.6-fold higher than the Ir anomaly in the K–Pg boundary layer at Gubbio and Caravaca, respectively, and 1120-fold higher than normal values in the continental crust. This enrichment in relation to the geochemical background could have resulted from the continuous depositions over these fluvial soils of the acidic waters draining this mining district over the centuries.

In the uppermost part of the soil, the profile can be differentiated in several horizons downwards: (i) a pale-greyish layer just below the layer of tailing (2–3 cm thickness); (ii) a reddish layer to 17–22 cm in depth; and (iii) a mixed layer composed by reddish areas (affected soil) and dark-brown areas (unaffected soil), between 22 and 42 cm in depth.

A systematic soil sampling was performed; just below the layer of tailings a hole 1 × 2 m and 1.2 m depth was dug and 3 of its walls were sampled. A sample was taken every 1 cm to a depth of 10 cm, then every 5 cm to a depth of 40 cm, and finally every 10 cm to a depth of 120 cm. All samples were numbered consecutively, but because of the large number of samples, only odd numbers were selected for this study. Tailings and soil were sampled in triplicate and analyses were made with the fine-earth fraction (<2 mm). The main physico-chemical properties related to element mobility in soils (pH, CaCO₃, texture) were analyzed; pH was determined potentiometrically in a 1:2.5 sample:water suspension in a Crison micropH 2002 instrument; CaCO₃ was measured according to the Bascomb (1961) method; and texture was analyzed by the pipette method (Loveland and Whalley, 1991). Total concentration of S and Fe was determined by X-ray Fluorescence after preparing soil pellets with lithium tetraborate 0.6:5.5 in a Philips PW-1404 instrument at the University of Granada; the analytical precision was better than 5%.

Total Ir and trace element concentrations were determined in finely ground soil samples (<0.05 mm) by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The analyses were made after acid-clean digestion in strong acids (HNO₃ + HF; ratio 2:3) at high temperature and

pressure in a Teflon-lined vessel. The spectrometer was equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining 1 mL min⁻¹ sample uptake rate), a cross-flow type pneumatic nebulizer and a double pass Scott-type spray chamber. All ICP-MS standards were prepared from ICP single element standard solutions (Merck quality) after appropriate dilution with 10% HNO₃. For calibration, two sets of multielement standards containing all the analytes of interest at five levels concentrations were prepared using Rhodium as internal standard. Procedural blanks for the estimation the detection limits ($3 * \sigma$; $n = 6$) were <0.03 ppb for Ir, <0.01 ppb for Cu, <2.68 ppb for Zn, <0.75 ppb for As, and <0.72 ppb for Pb. The analytical precision was better than ±5% in all cases.

Selective extractions were made to study the mobilization of Ir, and to evaluate the sorption and desorption of this element in relation to the main constituents of the soil. This procedure is extensively used in the study of trace elements in soil (Beckett, 1989) and previously applied to Ir speciation in relation to the K–T boundary (Dai et al., 2000; Premovic et al., 2006). Five reagents were used in this study: (i) extraction with water (W) was considered as soluble fraction (Sposito et al., 1982); (ii) extraction with calcium chloride (CA) was related to the exchangeable fraction (McLaren and Crawford, 1973); (iii) extraction with acetic acid (AC) was related to carbonates, and specifically linked to oxides and organic matter (McLaren and Crawford, 1973; Beckett, 1989); (iv) extracted with ethylenediaminetetraacetic acid (EDTA) was considered as bounded to carbonates, inorganic precipitates, amorphous oxides and organic ligands (Sposito et al., 1982; Beckett, 1989); and (v) extracted with oxalic-oxalate (OX) was specifically linked to oxides (Ure, 1995). The extraction power of these reactants is as follows: W < CA < AC < EDTA < OX; and a solution is able to extract forms in the previous solution (Ure, 1995). These extractions were analyzed by ICP-MS in a PE SCIEX ELAN-5000A spectrometer. Instrumental drift was monitored by regularly running standard element solutions between samples. The low matrix content of the column eluants meant that matrix effects and resulting drift was generally insignificant.

Statistical analyses of the data were made with SPSS v.15.0 software, one-way analysis of variance (ANOVA), Tukey's test, and Spearman correlation coefficient were used; the significant differences were considered when $p < 0.05$.

3. RESULTS

The distribution in depth of Ir and other elements into the soil matrix (Fig. 2) showed the maximum concentration next to the surface, where the layer of tailing was deposited. In the same figure, a certain redistribution of the elements throughout the profile can also be observed, although with different behavior depending on the considered element. The distribution pattern of Ir resembled that of Pb and As, with the maximum concentration being found just below the layer of tailings and a sharp decrease in the uppermost centimeters of the soil. Other elements, such as Cu and

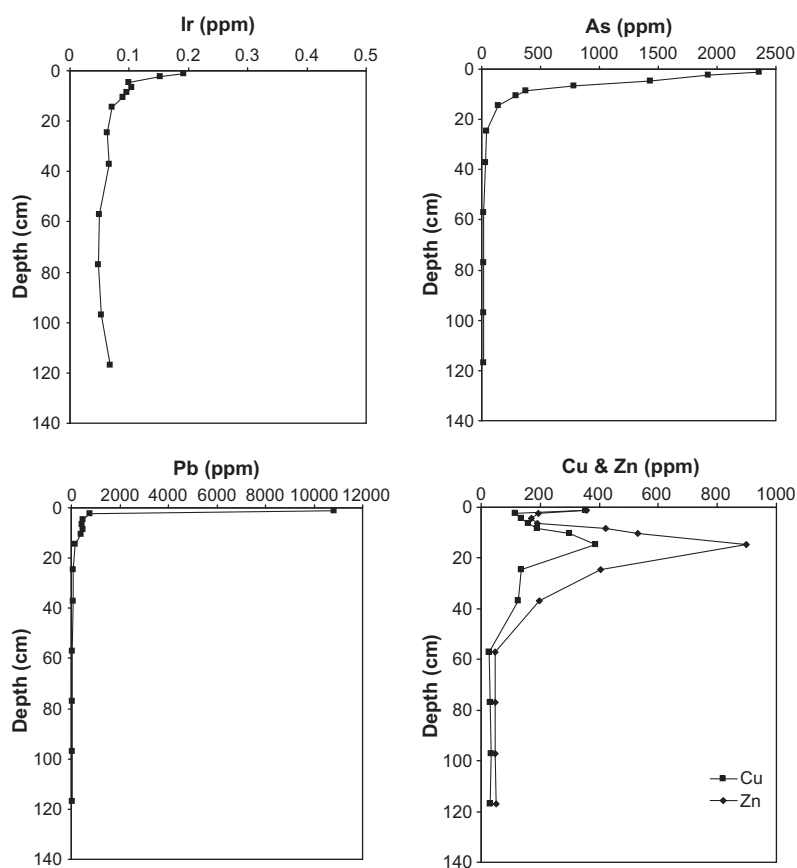


Fig. 2. Distribution in depth within the soil profile of Ir and other elements contained in the pyrite tailings.

Zn, showed a different distribution in depth pattern, with high concentration in the surface sample, a sudden decrease in the uppermost centimeters, and a strong increase in depth, with values even higher than the reached just below the layer of tailing.

In the case of Ir, the maximum concentration in soil was found in the uppermost 2 cm (0.192 ppm), although between 2 and 3 cm in depth the concentration was 3-fold higher than in the same levels of unaffected soil. Anomalous values of Ir were detected to 11 cm below the layer of tailings, this anomaly being considered when the concentration in the soil reached statistically significant differences ($p < 0.05$) in relation to the background concentration. As and Pb had the maximum concentration (2360 and 10846 ppm, respectively) in the uppermost 2 cm of the soil, with anomalous values detected to 40 cm in depth. Cu and Zn presented the maximum concentration (388 and 897 ppm, respectively) at 15 cm below the layer of tailing, with anomalous values detected to 55 cm in depth.

The variation in the concentration of the main elements in the pyrite tailings over time (Table 1) indicates different behavior between them. Iridium concentration decreased from the tailings after oxidation, reducing its values from 0.349 to 0.139 ppm after 10 years. Other elements also decreased their concentration from the tailings during this period with reductions for Zn from 6922.6 to 1415.1 ppm, for Cu from 2009.1 to 333.3 ppm, and for As from 3859.6

to 2803.2 ppm, in relation to the initial concentration in the tailings. Pb showed a relative increase over time, the concentration in the original tailing was 9507.3 and increased to 12721.2 ppm 10 years later. The release of these elements from the pollutant layer sharply increased their values in the uppermost part of the soil (Table 1) in relation to the background concentration. Iridium was retained mainly in the upper part of the soil, next to the layer of tailings, with a mean concentration of 0.129 ppm (2.3-fold the background concentration in the area). As, Pb, and Cu were also strongly retained in the upper part of the soil, with concentrations rising 45-, 28-, and 5-fold, respectively, over background values. Zn was the element least retained in this part of the soil, with a concentration 1.7-fold higher than the background values of the soil.

Selective extractions were made to study the forms in which Ir can be mobilized in the soil (Fig. 3). The residual fraction of Ir (not solubilized with any extractant) was >90% of the total soil concentration in all cases, indicating the insoluble forms of Ir were dominant in this media. The Ir soluble in water (W) was only detected in the uppermost 2–3 cm of the soil (pale-greyish layer), solubilizing 1.5% of the total Ir in this layer (0.0028 ppm). The forms extracted with calcium chloride (CA) were below the detection limits in all the samples analyzed. The oxalic-oxalate (OX) extracted the higher amounts of Ir in relation to the other extractant; being this form dominant in the part of the soil

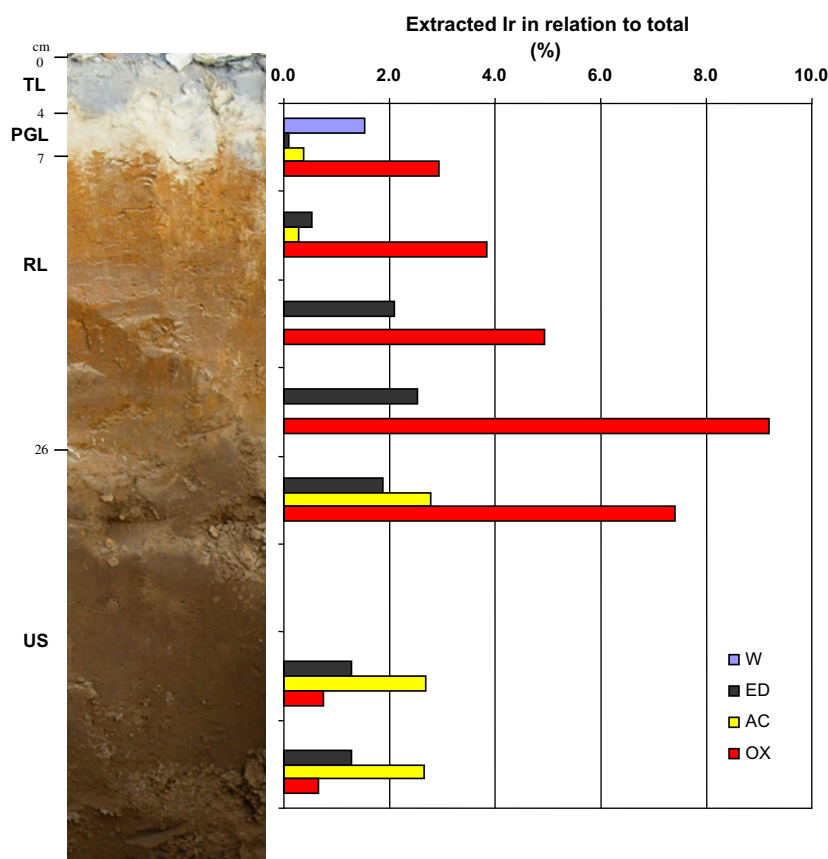


Fig. 3. Percentage of extracted Ir in relation to total concentration in soil. TL, tailing layer; PGL, pale-greyish layer; RL, reddish layer; US, unaffected soil. (Selective extractions: W, water; ED, EDTA; AC, acetic acid; OX, oxalic-oxalate.)

affected by the oxidative weathering of the pyrite tailings (reddish layer). The maximum extraction of Ir by OX were detected next to the bottom part of the reddish layer, with values around 9% of the total Ir in this part of the soil. The extraction of Ir by EDTA (ED) indicated the same increase towards the bottom part of the reddish layer than the Ir (OX) forms, although the total concentration extracted by ED were lower in all cases. Finally, when the unaffected soil became predominant, the Ir forms extracted by acetic acid (AC) were dominant in relation to the other extractant; being the values around 2.7% of the total Ir in the unaffected part of the soil.

4. DISCUSSION

The distribution in depth of Ir and other elements into the soil matrix (Fig. 2) indicates redistribution throughout the profile in relation to the change in the physico-chemical properties of the soil. The distribution pattern of Ir resembled that of the less mobile elements, such as Pb and As, with the maximum concentration being found just below the layer of tailings; other elements, such as Cu and Zn, showed high mobility after the oxidative weathering of the tailings.

The oxidative weathering of pyrite causes the release of elements bound to sulfides, and lowers the concentration of

these elements in the tailings (Table 1). Iridium was greatly leached from the tailings after oxidation, reducing its concentration after 10 years by as much as 60% in relation to the original values. Other elements mobilized from the tailings after 10 years were Zn, Cu, and As, with reductions of 80%, 83%, and 27%, respectively, in relation to the initial concentration. Pb proved to be the least mobile element, showing a relative increase over time (34%) by the depletion of the other elements in the tailings. The release of these elements from the pollutant layer sharply increased their values in the uppermost part of the soil in relation to the background concentration. Ir, As, Pb, and Cu was retained mainly in the uppermost 10 cm of the soil, meanwhile Zn was the element least retained in this part of the soil, being partially leached from the upper part of the soil. These changes are directly related to the oxidation reactions of pyrite and other sulfides (Nordstrom, 1982), and the oxidation rate depended mainly on the grain size, the concentration of dissolved O_2 , and microbial activity (Raiswell et al., 2009).

The main properties and constituents of the soil were correlated with the Ir concentration indicating a significant Spearman correlation coefficient with sulfur (0.934), iron (0.857), clay content (0.742) and pH (-0.869). Therefore, the mobility and distribution of Ir in depth within the soil profile should be directly related to the sulfur and iron re-

leased after the oxidation of the pyrite, and the texture of the soil (mainly the clay content), and inversely related to the strong acidification caused by the oxidative weathering. The regression analysis between Ir and these variables has statistically significant coefficients only with the clay percentage; in this case, the samples analyzed showed a good fit (Fig. 4), with the exception of the uppermost samples of the soils (0–3 cm), which were directly affected by the continuous leaching of the tailings. The equation indicates that around 50% of Ir concentration in the soil (0.026 ppm) was retained by the textural influence of the fine fraction, which reduces the infiltration of the soil solution in depth.

The original depositional environment in the K–T layers was different from the terrestrial media in this study, although in our case we found very important similarities. In both cases the Ir is related to high concentration of other metal(oid)s and pyrite, the local conditions were acidic, the waters had high concentration in sulfates, and the initial reactions occurred under anoxic conditions (with the tailings saturated in water). This situation could be similar to those determining the presence of Ir in sedimentary environments because the occurrence of this element is also related to precipitation as sulfides from sea water in anoxic/reductive conditions, and commonly associated to pyrite (Dolenec et al., 2000; Premovic et al., 2006). Anyway, the change in the conditions, mainly to oxidative media, implies that application to the K–T model should be made carefully and only related when the layers of K–T emerge to terrestrial environment.

Selective extractions indicated that the residual fraction of Ir (not solubilized with any extractant) was >90% of the total soil concentration in all cases; therefore, the insoluble forms dominated, indicating the low mobility of Ir in this media. The only part of the soil where the Ir was detected as soluble in water (W) was in the uppermost 2–3 cm of the soil (pale-greyish layer), this coincided with the part of the soil that received the acidic solutions directly from the oxidation of the tailings. The absence of forms extracted with calcium chloride (CA) indicated that Ir retention by the exchangeable complex of the soil (mainly electronegative particles of colloidal phyllosilicates and organic matter) was negligible; in this case, the retention of Ir within the soil matrix should not be related to adsorption processes of cationic forms. The forms extracted with oxalic-oxalate (OX) were dominant in the part of the soil affected by the oxida-

tive weathering. Therefore, the retention of Ir in this part of the soil could be related to the amorphous iron forms (mainly electropositive colloidal particles) dissolved by the oxalic-oxalate. In this case, the retention of Ir within the soil matrix should be related to anionic forms linked to or occluded in the amorphous oxides of the soil. Increased Ir (OX) was detected towards the bottom part of the reddish layer, coinciding with the increase of the amorphous iron forms described by García et al. (2009) in this type of soil. The extraction of Ir by EDTA (ED) indicates that part of the forms retained by amorphous iron oxides are easily complexable by this extracting agent, showing the same increase towards the bottom part of the reddish layer. Finally, the Ir forms extracted by acetic acid (AC) were dominant in the unaffected part of the soil, indicating that precipitation of Ir in the soil could be related to the calcium carbonate content, both by the rise in pH triggered by the carbonates as well as by co-precipitation processes.

The obtained results, evidencing the relatively mobile behavior of Ir into the sediments in depth reveals especially interesting when analyzing Ir anomalies registered in the fossil record. As previously introduced, usually high concentrations of iridium in sediments have been related to impact-events, most of them associated to different order mass-extinctions. Iridium data were used by researchers to interpret the impact event, including the characterization of impact features (see Section 1). However, according our research, original Ir abundance could be secondarily modified, and then a direct analysis of the iridium values recorded in sediments could induce misinterpretations. We considered the here conducted work as a first step when comparing with the fossil record, taking into account that the modern example studied represents only a particular case, revealing the mobility of Ir in terrestrial sediments belonging to soils developed on land, while Ir anomalies, as those associated with the K/Pg impact-boundary mass-extinction, are recognized in a wide variety of depositional settings. However, the comparison between the actual example and the fossil record can be considered as a valuable approach, especially for Ir data belonging to terrestrial settings. Even K–Pg Ir anomalies were initially discovered in marine rocks (Alvarez et al., 1980), also are registered in numerous K/Pg boundary sections from continental sediments deposited under freshwater conditions (Orth et al., 1981; Pillmore et al., 1984; Tschudy et al., 1984), including paleosols spanning the K–Pg transition (Fastovsky, 1987; Fastovsky and McSweeney, 1987; Retallack et al., 1987; Fastovsky et al., 1989; Retallack, 1996, 2004).

5. CONCLUSIONS

The oxidative weathering of pyrite tailings deposited over the soil during a catastrophic mining spill in 1998 caused the release and infiltration into the soil of anomalous Ir concentrations, with values of up to 0.192 ppm in the uppermost 2–3 cm of the soil. The distribution in depth of the Ir concentration revealed mobility of this element through the soil matrix, with anomalous values detected to 11 cm in depth. The main constituents and soil properties related to the distribution in depth of Ir were sulfur, iron, clay content, and pH. The acid-

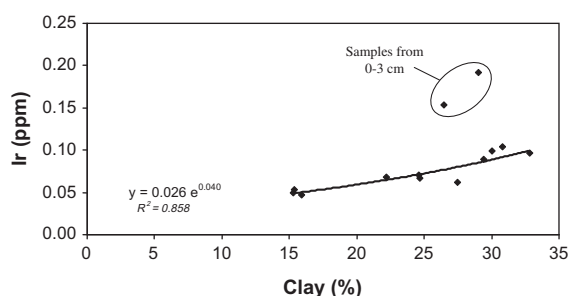


Fig. 4. Regression analysis between Ir concentration and clay content in the soil.

ification of the uppermost part of the soil was presumably related to the initial infiltration of Ir, and the textural influence of the fine fraction (clay), by reducing the infiltration rate of the soil solution, may have determined the redistribution of this element in the soil.

Selective extractions of Ir indicate that the residual/insoluble fraction was dominant throughout the soil (>90% of the total Ir). Concentrations of water-soluble Ir (1.5% of the total) were detected in the uppermost part of the soil, and this was directly affected by the leaching of acidic waters coming from the oxidation of the pyrite tailings. Oxalic-oxalate extraction of Ir was the dominant fraction in the affected part of the soil (reddish layer), with concentrations exceeding 9% of the total Ir in the bottom part of this weathered layer. Therefore, Ir retention in this media could be related to the amorphous iron forms dissolved by this extracting agent.

These results support the relatively mobile behavior of Ir within the sediments in depth under certain conditions, despite that this element is traditionally considered to have low mobility. This is of special interest in the study of Ir-bearing horizons in the fossil record, such as those associated with impact-related mass-extinction events, preventing misinterpretations based exclusively on Ir concentrations. Anyway, the selective extraction of Ir used in this work was a valuable tool for relate the main forms in which Ir is retained by the main constituents of the soil, but further studies are necessary focused in the speciation of Ir both in reducing as in oxidative conditions, to advance in the knowledge and mobility of this element in sedimentary environments and to attain more accuracy in the studies involving implications of this element in the fossil record.

ACKNOWLEDGMENTS

This research was supported by the Ministerio de Ciencia e Innovación of the Spanish Government (Project CGL2008-03007), and by the Junta de Andalucía (Project RNM-3715, and the Research Group RNM-178).

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Associate editor: Johnson R. Haas