

Osmium, tungsten, and chromium isotopes in sediments and in Ni-rich spinel at the K-T boundary: Signature of a chondritic impactor

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Abstract—It is now established that a large extraterrestrial object hit the Earth at the end of the Cretaceous period, about 65 Ma ago. We have investigated Re-Os, Hf-W, and Mn-Cr isotope systems in sediments from the Cretaceous and the Paleogene in order to characterize the type of impactor. Within the Cretaceous-Tertiary (K-T) boundary layer, extraterrestrial material is mixed with terrestrial material, causing a dilution of the extraterrestrial isotope signature that is difficult to quantify. A phase essentially composed of Ni-rich spinel, formed in the atmosphere mainly from melted projectile material, is likely to contain the extraterrestrial isotopic signature of the impactor. We show that the analysis of spinel is indeed the best approach to determine the initial isotope composition of the impactor, and that W and Cr isotopes confirm that the projectile was a carbonaceous chondrite.

INTRODUCTION

The Cretaceous-Tertiary boundary (hereafter termed K-T boundary, although strictly the Cretaceous-Paleogene, or K-P boundary) corresponds to a mass extinction, in particular to the extinction of dinosaurs, numerous ammonites, and planktonic foraminifera (Russell 1979; Smit 1982; Buffetaut 1984). Two theories exist to explain this major biological crisis 65.5 ± 0.3 Ma ago: 1) a collision of the Earth with an asteroid or a comet (e.g., Alvarez et al. 1980; Kyte 1998), and 2) a giant volcanic eruption (Officer and Drake 1983) that gave birth to the Deccan flood basalts (e.g., Courtillot et al. 1986; Hofmann et al. 2000). It is now well established that both events occurred at that time—more precisely, giant volcanism started 66.5–67 Ma ago, stopped, and resumed shortly after the K-T boundary (Hofmann et al. 2000)—but their respective contributions to the observed environmental and biological events are still a subject of debate. The aim of the present paper is not to discuss which phenomenon is responsible for the mass extinction, but to identify the nature of the extraterrestrial object that hit the Earth at that time.

All over the world, the K-T boundary is associated with the same identifying markers, even if not all of them are always present at each site: high concentration in Ir and other siderophile elements, presence of shocked quartz and impact glass particles. Highly oxidized Ni-rich spinel crystals of an unusual composition have also been found at several sites (Kyte and Smit 1986; Robin et al. 1992; Kyte and Bostwick 1995; Robin and Rocchia 1998). The spinel crystals have a dendritic, skeletal cruciform, or octahedral morphology, that is characteristic of rapid crystallization and cooling from a high-temperature melt.

Because of the high siderophile element contents of the K-T boundary sediments, Kyte et al. (1980, 1985) first suggested that the impactor was probably an iron meteorite. But the abundance ratios of siderophile elements in the K-T boundary clays alone are not sufficient to distinguish between the different possible extraterrestrial sources. A cometary fragment has also been mentioned as a possible impactor (Hsü 1980). According to numerical simulations (Pierazzo and Melosh 1999), several percent of the material originating from the impactor could have survived without melting. A fossil meteorite was found in the K-T sediments of a site in

the Northern Pacific (DSDP Hole 576), which also contained magnetoferrite spinel grains. This meteorite may be a fragment of the impactor, although it is impossible to ascertain if it was accreted as part of the K-T projectile (Kyte 1998). Geochemical and petrographical analysis of this sample indicated that it is likely derived from a metal- and sulfide-rich carbonaceous chondrite (4–8% metal and sulfides; presence of iron oxides) (Kyte 1998). This conclusion confirmed those of Alvarez et al. (1982) who suggested a chondritic impactor, based on the quasi-chondritic distribution of siderophile elements in the sediments of the K-T boundary.

Given that the different classes of meteorites can be distinguished by specific isotopic ratios, strong constraints on the nature of the impactor can be obtained by comparing the isotopic signatures of K-T boundary sediments to those of different types of meteorites. Several isotopic studies have already been carried out in the past on sediments collected at different K-T sites. Neither strontium (Sr) (Shaw and Wasserburg 1982; DePaolo et al. 1983; Meisel et al. 1995; Frei and Frei 2002) nor lead (Pb) isotopes (Dia et al. 1989; Frei and Frei 2002) provide any indication concerning the nature of the impactor. Strontium and Pb isotope data indicate both a modification of erosional sources and enhanced weathering, but are useless when assessing the composition of the extraterrestrial bolide.

The rhenium-osmium couple (Re-Os), involving two siderophile elements, has also been extensively studied (Luck and Turekian 1983; Lichte et al. 1986; Meisel et al. 1995; Frei and Frei 2002). Extraterrestrial objects are characterized by an Os isotopic composition similar to that of the terrestrial mantle ($^{187}\text{Os}/^{188}\text{Os} \sim 0.12$) (Luck et al. 1980) but very different from that of the continental crust ($^{187}\text{Os}/^{188}\text{Os} = 1.26$) (Esser and Turekian 1993). Contrary to the situation for Pb and Sr, the mass balance is favorable to detect an extraterrestrial input because continental rocks are Os-poor and radiogenic, whereas meteorites are Os-rich and unradiogenic. Lichte et al. (1986) and Meisel et al. (1995) measured an Os isotopic composition in K-T boundary sediments that was slightly more radiogenic than that of chondrites, whereas Luck and Turekian (1983) concluded, after correction related to the in situ radioactive decay of Re (^{187}Re half-life = 41.6 Gyr) (Lindner et al. 1989), that the impactor was probably a pallasite or an iron meteorite. Studying a whole profile, Meisel et al. (1995) demonstrated that the K-T boundary has an Os isotope composition that does not fit a smooth terrestrial evolution curve for the Os isotope stratigraphy. It is still important to determine whether the isotopic signature is identical for several marine sites or if physico-chemical conditions during sedimentation may have played a role in producing the observed Os isotope stratigraphy. To do so, it is necessary to establish the concentration profiles for different sites, as we have done here and as has also been done for the Stevns Klint

K-T boundary site by Frei and Frei (2002) in parallel to our own investigations. Frei and Frei (2002) observed a pronounced drop in $^{187}\text{Os}/^{188}\text{Os}$ in the K-T sediments relative to the composition of the sediments deposited directly prior to the K-T event and, conflicting with Luck and Turekian (1983), showed that the K-T impactor was chondritic from the $^{187}\text{Os}/^{188}\text{Os}$ ratios measured in the most platinum group element (PGE) enriched horizon of the K-T boundary clay.

Based on the Cr concentration in the sediments, Shukolyukov and Lugmair (1998) concluded that the Cr from the K-T boundary is almost exclusively of cosmic origin. Samples from both the Stevns Klint and Caravaca boundary sites have the same Cr isotopic composition (Shukolyukov and Lugmair 1998), which is characteristic of carbonaceous chondrites, again supporting previous evidence for a chondritic impactor (Alvarez et al. 1980; Kyte et al. 1980; Alvarez et al. 1982; DePaolo et al. 1983). These Cr isotopic compositions were the first coherent isotopic results from different K-T sites that provided clear constraints on the nature of the projectile. Recently, Trinquier et al. (2006) measured Cr isotopes in sediments from Stevns Klint and Raton Basin (Colorado/New Mexico, USA) and confirmed the results of Shukolyukov and Lugmair (1998). An alternative impactor may have been a cometary bolide, since comets most likely consist of material similar to carbonaceous chondrites (e.g., Weissman 1986; Gombosi and Houppis 1986). However, few isotopic measurements of cometary material exist so far to validate this hypothesis, with existing data only published for lighter elements.

With the present study, we tested the hypothesis that the impactor was a carbonaceous chondrite using different isotopic systems. Given that the K-T boundary sediments are enriched in siderophiles (Alvarez and Lowrie 1977; Ganapathy 1980; Smit and Hertogen 1980), we chose the siderophile elements Os and W. Other elements aside from Cr are useful in evaluating the degree of mixing that occurred between extraterrestrial material and the surrounding terrestrial sediments, resulting in disturbed isotopic ratios. In order to avoid this potential mixing problem, we analyzed a phase highly enriched in cosmic components. Nickel-rich spinel is a magnetic mineral formed by oxidation of meteoritic material at high temperature (Robin et al. 1992; Gayraud et al. 1996; Toppani and Libourel 2003). It differs from terrestrial spinel in its high Ni content, reflecting the high abundance of this element in meteorites, and a high ferric/ferrous iron ratio resulting from crystallization in an O_2 -rich environment. This mineral is typically found in meteoroid ablation material (Robin et al. 1992) and in a variety of impact debris in the sedimentary record: at the K-T boundary (Smit and Kyte 1984; Kyte and Smit 1986; Robin et al. 1991; Robin et al. 1993; Kyte et al. 1996; Rocchia et al. 1996; Robin and Rocchia 1998), in

Table 1. Details of sample locations.

Name of the site	Name of the sample	Relative position (cm)	Comments
Bidart	B 7	-45 to -40	
	Clays	0 to +0.5	
	B25	+33 to +38	
Caravaca	CAR 22	-16 to -11	The ochre layer of the K-T boundary is extremely thin. The sample contains both ochre clay and some gray clay from the layers immediately above.
	CAR 26	0 to +0.5	
	CAR 13	+20 to +25	
Stevns Klint	SK 111	-20 to -15	The transition between the gray clay and the white limestone is clearly visible a few mm below the upper edge of the sample.
	SK 202	0 to +1	
	SK 203	+1 to +2	
	SK107	+20 to +30	

The position of each sample is calculated relative to the basement of the K-T boundary layer.

Upper Eocene sediments worldwide (Glass et al. 1985; Pierrard et al. 1998; Pierrard 1999; Pierrard et al. 1999; Vonhof and Smit 1999), in a Lower-Middle Jurassic hardground from the southern Alps in Italy (Jehanno et al. 1988), in Late Pliocene sediments from the Antarctic basin (Margolis et al. 1991), and in Oligocene sediments from the central North Pacific (Kyte and Bostwick 1995). Two potential sources for the K-T impact spinel are vapor condensate (Bohor et al. 1986; Kyte and Smit 1986; Kyte and Bostwick 1995; Ebel and Grossman 2005) and projectile ablation debris (Kyte and Smit 1986; Robin et al. 1992; Gayraud et al. 1996). Although there is no consensus about the mode of formation of the K-T spinel (see the nickel-rich spinel section), its high Ni content argues for a predominant derivation from projectile material (Bohor et al. 1986; Robin et al. 1992). Its study can thus constrain the nature of the K-T impactor. Results have already been presented in a preliminary report (Quitté et al. 2003).

DESCRIPTION OF THE SAMPLING SITES AND OF THE SAMPLES

We focus on three K-T boundary sites: Stevns Klint in Denmark, Caravaca in Spain, and Bidart in France. All three are marine successions. Few isotopic studies have been carried out thus far on Bidart samples. The sampling procedure was described by Rocchia et al. (1987). Sampling was performed using plastic tools (to avoid contamination from stainless steel) and samples were stored separately in glass containers in a dry environment. A brief description of the K-T clay layer at each outcrop is given below. For more detailed description of the K-T boundary sites (outcrop location, lithology, biostratigraphy, mineralogy, and trace element stratigraphy), the reader is referred to the references provided below. In each case, we have analyzed sediments from the K-T boundary itself as well as sediments below and above the boundary (Table 1) to clearly distinguish the signature of the boundary from the mean value of the environment.

Stevns Klint (Denmark)

The K-T boundary at this site is composed of a layer of gray clay with thin ochre veins of iron hydroxides and pyrite (Jehanno et al. 1987). Between the bottom of the clay layer and 5 cm above, pure and well-crystallized smectite is present. This smectite is highly enriched in Ir (up to 100 ppb, which corresponds to 20% of the chondritic content) (Rocchia et al. 1987; Bauluz et al. 2000) compared to the underlying and overlying layers (less than 1 ppb) and may originate from alteration of an originally glassy material (Jehanno et al. 1987). Above the boundary, the *Danian* sediments are white-yellow limestone containing *Cerithes* (gastropods) fossils, while the uppermost Cretaceous is represented by white chalk.

Caravaca (Spain)

The K-T boundary at this site corresponds to a very thin layer of ochre clays that contain up to 70 ppb Ir. Basal layers of the boundary section are light gray or green limestone, below a thin ferriferous layer and 8 to 9 cm of clays with various shades of gray (Dia et al. 1989), overlain by a beige limestone (e.g., Smit 1979; DePaolo et al. 1983; Jehanno et al. 1987; Rocchia et al. 1987).

Bidart (France)

The late Cretaceous (Maastrichtian) sediments are gray-beige marls. The K-T boundary at this site is marked by ochre clays that contain 5 ppb Ir and about 4000 Ni-rich spinel crystals per milligram, and is overlain by pink-orange limestone (Delacotte 1982; Bonté et al. 1984; Jehanno et al. 1987; Rocchia et al. 1987). In contrast to the other sites, it does not contain any smectite (Jehanno et al. 1987). Scarce sulfides are dispersed in the sediments that have not been encountered at other sites, indicating a continuous reducing environment at the Bidart site, in contrast to Stevns Klint and Caravaca. At the two latter sites, authigenic sulfides have

subsequently been oxidized to goethite that now defines the so-called “K-T red level” (Robin and Rocchia 1998).

The Nickel-Rich Spinel

We analyzed spinel crystals from the Bidart section that come from a 2–3 cm thick clay layer overlying the Maastrichtian limestones. The stratigraphic distribution of the spinel grains is spread over 10–15 cm. Three possible formation processes have been proposed for the K-T spinel:

1. Direct condensation from vaporized projectile and target material (Bohor et al. 1986; Ebel and Grossman 2005);
2. Crystallization in liquid droplets condensed from the impact vapor cloud (Kyte and Smit 1986; Kyte and Bostwick 1995); and
3. Crystallization in liquid droplets generated by ablation of impact debris (Robin et al. 1992; Robin et al. 1993).

Spinel condensation in the impact vapor cloud is considered unlikely because conditions there are highly reducing (Gayraud 1995; Gayraud et al. 1996; Siret 2004). Rather, the K-T spinel was formed by high-velocity interaction of impact debris with the terrestrial atmosphere (Robin et al. 1992; Robin et al. 1993; Gayraud et al. 1996; Robin and Rocchia 1998; Siret and Robin 2003), when impactor debris are slowed down at low altitude (less than 20 km) and high oxygen fugacity ($fO_2 > 10^{-2}$ bar and $T < 1550$ °C) (Gayraud et al. 1996), but $T > 900$ °C (Kyte and Smit 1986). Such conditions of temperature and oxygen fugacity do not occur during volcanic processes because terrestrial magmas evolve under environments with an extremely low oxygen fugacity (Robin et al. 1992; Gayraud et al. 1996). The high Ni content in spinel grains from the K-T boundary also excludes the formation of this mineral from crustal material that is highly depleted in Ni (<0.1 wt%) and indicates instead a meteoritic source (chondrites, for example, contain more than 1 wt% Ni).

In general, the composition of ablation spinel varies according to the oxygen fugacity (Robin et al. 1992). The oxidation state ($Fe^{3+}/total\ Fe$) increases from micrometeorites to ablation materials and impact products, corresponding to an increase of the oxygen fugacity because of decreasing altitudes at the time of crystallization. During an impact, spinel is formed at low altitude and is thus almost completely oxidized ($Fe^{3+}/total\ Fe = \sim 100\%$). The composition of spinel found at European K-T sites is characteristic of spinel from meteorite fusion crusts and meteoritic ablation particles ($Fe^{3+}/total\ Fe = 75\text{--}90\%$), but the composition strongly differs from that of spinel found in micrometeorites, whose Ni content and Fe oxidation state are lower (Ni: 1–2% and $Fe^{3+}/total\ Fe = 65\text{--}75\%$) (Robin et al. 1992; Robin and Rocchia 1998). There are some discrepancies between K-T spinel and the impact products found in the marine environment, whose oxidation state is higher ($Fe^{3+}/total\ Fe > 90\%$), and between K-T spinel and normal terrestrial spinel that is characterized by an Fe oxidation state lower than 70% (Robin et al. 1992; Robin and

Rocchia 1998). K-T spinel from European sites is thus most likely derived from ablation product of projectile debris. Nevertheless, Kyte and Bohor (1995) showed shifts in the composition between spinel from the K-T boundary on Pacific sites and meteoritic ablation particles. Pacific K-T spinel crystals are all highly oxidized and probably correspond to impact products.

Whatever the spinel formation scenario might be, this mineral is most likely a relict of the K-T impactor. For some authors, the spinel crystals constitute a mineralogical marker specific to the meteoritic material melted and oxidized at high temperature in the terrestrial atmosphere (Robin and Rocchia 1998), while for others they correspond to the material that first accreted in the impact cloud at high temperature from a part of the cloud strongly enriched in material coming from the projectile (Kyte et al. 1996). The K-T spinel is therefore expected to carry the true isotopic signature of the impactor, especially given that it is not affected by diagenesis (Robin and Molina 2006). Thus the Ni-rich spinels are the only relict crystals available to constrain the composition of the impactor at the K-T boundary (Kyte and Smit 1986).

ANALYTICAL PROCEDURE

Nickel-Rich Spinel Crystals

Spinel crystals were separated from the Bidart sediments with a magnet following the procedure described in Robin and Molina (2006). Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analysis of a fraction leached for 30 min in 27N HF revealed the proportions of minerals to be 20% silicates and 80% spinel. Among the latter, 75% are of cosmic origin and 25% are terrestrial (15% magnetite, 9% titanomagnetite, and 1% chromiferous-magnetite). The EDS analysis yielded the following composition for the spinel fraction: 10.5 wt% MgO, 3.8 wt% Al_2O_3 , 0.3 wt% TiO_2 , 5.4 wt% Cr_2O_3 , 0.6 wt% MnO, 11.1 wt% FeO, 63.9 wt% Fe_2O_3 , 4.4 wt% NiO, and an $Fe^{3+}/total\ Fe$ ratio of 83.9 (Robin and Rocchia 1998). To ensure we get the true isotopic composition and concentration of spinel and not those of a mixture between spinel crystals and sediments, we performed two successive leaches in HF (2 h in 1N HF followed by 30 min in 27N HF) that dissolved almost completely the remaining silicates and carbonates.

Rhenium-Osmium

Samples were first crushed in an agate mortar. About 500 mg of the powdered sample (only 50 mg for the Os-rich boundary itself) were digested in a HF-HBr mixture after addition of a Re-Os spike. For spinel, the available mass was about 0.6 mg. No special procedure was required to completely dissolve this mineral, which could be digested in HF-HBr like the sediment samples. It was not possible

without further analytical development to combine the Re-Os separation chemistry with that of other elements (W and Cr) because the medium must remain reducing to scavenge Os as $\text{Os}(\text{Br})_6^{2-}$. We therefore had to work on two aliquots. Re-Os separation and further purification were carried out following the method described in Birck et al. (1997). The Os isotopic compositions as well as the Re and Os concentrations were determined by isotope dilution using negative thermal ionization mass spectrometry (N-TIMS), as detailed by Birck et al. (1997).

Tungsten

About 400 mg of the powdered sample (150 mg for the boundary itself) were dissolved in an HNO_3 -HF-HCl mixture at 145 °C for 48 h (Quitté et al. 2002). Clay samples and limestone are easily digested. Spinel grains are known to be difficult to dissolve, but only a small mass (about 1 mg) was available and digestion in a few milliliters of an HNO_3 -HF-HCl mixture proved efficient. No special dissolution procedure was required. After digestion, the sample solution was evaporated and the residue taken up twice in 6N HCl. Boric acid was added to get rid of the precipitate of calcium fluoride and the solution was once again evaporated. The tungsten extraction consisted of a two-step ion-exchange procedure on a column filled with an anion resin (Quitté et al. 2002). The last elution fraction was evaporated, taken up in diluted HF, and loaded on an Ir filament. Sulfuric acid and a mixture of MgNO_3 and NaNO_3 were added as an emitter for the determination of isotopic composition by N-TIMS, as detailed in Quitté et al. (2002). A spiked aliquot was used to determine the concentration.

Chromium

The Cr separation used the first eluted fraction from the W ion-exchange chromatography for a two-pass purification on cation-exchange resins (Rotaru 1992). The final solution containing Cr was evaporated and then taken up in diluted HCl before being loaded on a tungsten filament with a mixture of silica gel, boric acid, and aluminum to act as an emitter. The Cr isotopic composition was measured by TIMS following the method described by Rotaru (1992).

RESULTS

Osmium

Results are presented in Fig. 1 and Table 2. The K-T boundary is enriched in Os relative to the surrounding sediments, which is in good agreement with previous observations (e.g., Meisel et al. 1995; Frei and Frei 2002). The Os concentration in the sediments from the end of the

Cretaceous is of the same order of magnitude at all 3 K-T boundary sites, and is comparable to the results of Frei and Frei (2002), while the Os enrichment within the K-T layer is highly variable depending on the site: the relative enrichment is only 4-fold at the Bidart section, but amounts to a factor of about 130 at Stevns Klint and up to a factor of 250 at Caravaca.

The boundary layer also shows a Re enrichment, together with a lower Re/Os ratio relative to the surrounding sediments (Table 2). A lower Re/Os ratio at Caravaca and Stevns Klint compared to Bidart may be explained by a scavenging of Re in pyrites as Re is siderophile and chalcophile. Some pyrites are still present at Bidart, whereas this mineral has been altered and oxidized at Stevns Klint and Caravaca, allowing remobilization of Re. Thus the present Re/Os ratio may not correspond to the initial elemental ratio of the sediments, which hampers a precise, time-integrated Re correction. The Os isotopic composition of the sample 65 Ma ago may well have been less radiogenic than measured today.

In the clay from the K-T boundary at Stevns Klint we measured a lower $^{187}\text{Os}/^{188}\text{Os}$ ratio than Luck and Turekian (1983), but our value is close to that of Frei and Frei (2002). The $^{187}\text{Os}/^{188}\text{Os}$ ratios of the sediments at the end of the Cretaceous range from 0.274 to 0.297 for the sites analyzed here (Table 2). The ratio significantly decreases at the boundary itself and reaches values as low as 0.164 at Stevns Klint (Table 2; Fig. 1), compared to the least radiogenic value of 0.1485 measured in any K-T boundary deposit so far (Peucker-Ehrenbrink et al. 1995).

The Ni-rich spinel from Bidart contains 23 ppb Os, 50 ppb Re, and has a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.165, while the surrounding K-T boundary sediments contain 0.7 ppb Os, 0.9 ppb Re, and have an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.236. Thus, spinel is more than 30 times richer in Os and 50 times richer in Re than sediments from the boundary, and is characterized by a less radiogenic Os composition.

Tungsten

Like Os and Ir, W is also siderophile, but to a lesser extent. The K-T boundary is enriched in W relative to the surrounding sediments, with concentrations between 1.2 and 6.7 ppm (Table 3). Caravaca and Stevns Klint both present the same enrichment factor relative to the local sediments from the late Cretaceous and the early Paleogene (enrichment factor: 12–13), whereas the absolute concentrations are highly different at both sites (Table 3; Fig. 2). In contrast, the W concentration at the boundary in Bidart only increases by a factor of 2.

The W isotopic composition for the three sites is also presented in Fig. 2. All terrestrial samples have a so far unique W isotopic value of 0 $\epsilon(^{182}\text{W}/^{184}\text{W})$, where $\epsilon(^{182}\text{W}/^{184}\text{W})$ is the $^{182}\text{W}/^{184}\text{W}$ ratio of the sample relative to the terrestrial

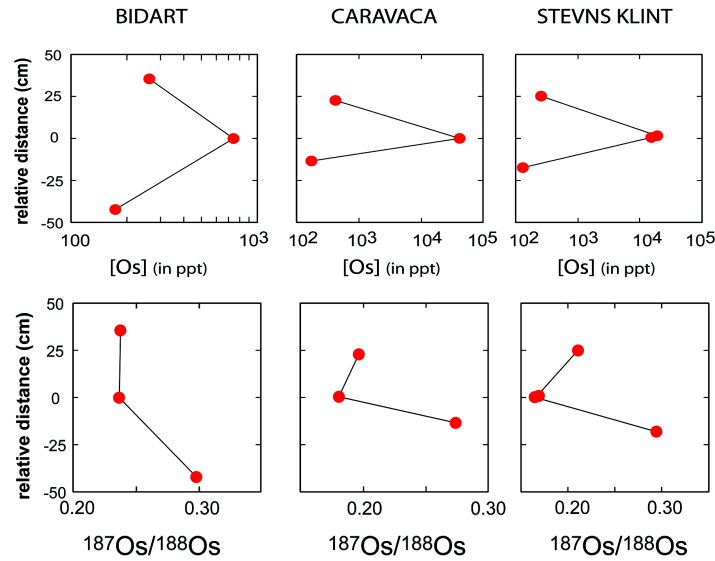


Fig. 1. Osmium concentration and $^{187}\text{Os}/^{188}\text{Os}$ ratio as a function of the distance to the K-T layer basement. The layer itself is enriched in Os and yields a lower $^{187}\text{Os}/^{188}\text{Os}$ than the surrounding sediments. The error bars are smaller than the symbols. Note the logarithmic scale for the concentration.

Table 2. Os isotopic composition and Os-Re concentrations in sediments and spinel from the K-T boundary transition.

	$^{187}\text{Os}/^{188}\text{Os} \pm 2\sigma$	Os (ppt)	Re (ppt)	$^{187}\text{Re}/^{188}\text{Os}$
Bidart				
B7	0.29722 ± 96	173	328	9.3
Clays	0.23639 ± 48	737	912	6.0
B25	0.23734 ± 48	261	464	8.6
Spinel crystals	0.16490 ± 84	23,086	50,369	10.3
Caravaca				
CAR22	0.27399 ± 84	169	599	17.3
CAR26	0.18058 ± 36	42,355	4011	0.5
CAR13	0.19651 ± 96	417	189	2.2
Stevens Klint				
SK111	0.29435 ± 36	133	646	23.8
SK202	0.16418 ± 24	15,523	8010	2.5
SK203	0.16897 ± 12	19,253	15,323	3.8
SK107	0.21088 ± 36	261	376	7.0

Isotopic ratios are normalized to $^{192}\text{Os}/^{188}\text{Os} = 3.0871$. The standard, prepared from $(\text{NH}_4)_2\text{OsCl}_6$ provided by Merck, has a $^{187}\text{Os}/^{188}\text{Os} = 0.17387 \pm 18$.

The Re standard is a NBS standard in HNO_3 medium. The Os and Re blanks (0.02 pg and 2.9 pg, respectively) are negligible. The 2σ errors refer to the last significant digits. The uncertainty on the concentration measurements is about 0.5%.

standard (a commercial ICP standard solution) in parts per 10^4 . The isotopic composition of sediments from both sides of the boundary cannot be distinguished from other terrestrial samples as expected. On each of the three sites, the boundary sample does not contain any resolvable W isotopic anomalies either.

Concentration and isotopic analysis of W in the Ni-rich spinel is a priori a powerful tool to provide strong constraints on the composition of the impactor because W is a refractory element and so losses by volatility at the time of impact are highly unlikely. The isotopic composition of these minerals must represent those of the impactor. Spinel crystals show a

deficit of $-1.7 \pm 0.5 \epsilon(^{182}\text{W}/^{184}\text{W})$ and the W concentration equals 1.9 ppm. Spinel is more depleted in ^{182}W and has a lower W concentration than the clays on the same site.

Chromium

Sediments from the Caravaca site were analyzed as Shukolyukov and Lugmair (1998) did, but we have also analyzed sediments from Bidart, focusing in particular on spinel. The magnetic fraction contains a maximum of 20% silicates and at least 60% cosmic spinel, 12% magnetite, 7.2% titanomagnetite, and 0.8% chromiferous magnetite. We can

Table 3. W isotopic composition and concentration in sediments and spinel from the K-T boundary transition.

	$\epsilon(^{182}\text{W}/^{184}\text{W}) \pm 2\sigma$	W (ppb)
Bidart		
B7	0.42 ± 0.77	1658
Clays	-0.56 ± 0.91	3281
B25	-0.13 ± 0.21	1115
Spinel crystals	-1.67 ± 0.47	1910
Caravaca		
CAR22	-0.08 ± 0.41	599
CAR26	0.58 ± 0.49	6692
CAR13	0.71 ± 0.51	560
Stevens Klint		
SK111	0.05 ± 0.42	88
SK202	-0.04 ± 0.70	1185
SK203	0.21 ± 0.43	987
SK107	-0.17 ± 0.22	88

Isotopic ratios are normalized to $^{186}\text{W}/^{183}\text{W} = 1.985935$. The isotopic composition is expressed using the ϵ notation, where ϵ is the deviation, in parts per 10^4 , of the normalized $^{182}\text{W}/^{184}\text{W}$ ratio of the sample from our terrestrial standard, a commercial ICP standard solution from Johnson Matthey Co. ($^{182}\text{W}/^{184}\text{W} = 0.864699 \pm 0.000008$). Blanks range from 30 to 50 pg and are negligible. The uncertainty on the concentration measurements is about 1%.

then calculate the percentage of extraterrestrial Cr present in the magnetic phase, assuming that cosmic spinel contains ~3.5% Cr (Robin and Rocchia 1998) and terrestrial chromiferous magnetites ~10% Cr. The Cr content of the other phases (silicates, magnetite, and titanomagnetite) is less than 0.1%. A simple mass balance calculation indicates that more than 95% of the Cr in the magnetic phase must be of extraterrestrial origin.

The Cr isotopic signatures of the K-T boundary samples from Caravaca and Bidart are identical, apparently depleted in ^{53}Cr by about 0.5 $\epsilon(^{53}\text{Cr}/^{52}\text{Cr})$ units (Table 4), using the same normalization procedure as Shukolyukov and Lugmair (1998). This result is in good agreement with previous data (Shukolyukov and Lugmair 1998; Trinquier et al. 2006) and confirms an extraterrestrial source of Cr. The spinel crystals from Bidart are also characterized by the same apparent depletion in ^{53}Cr [$-0.48 \pm 0.09 \epsilon(^{53}\text{Cr}/^{52}\text{Cr})$].

DISCUSSION

Osmium

Enrichment in Os and Re

The Os enrichment of the K-T boundary relative to the surrounding sediments cannot be the result of a decrease in sedimentation rate, as the Os isotopic composition of the K-T layer differs from that of the late Cretaceous and early Paleogene. The enrichment can thus only be explained by an "exotic" input of Os. The Os concentration is about 15 ppt in the Deccan Traps (Allègre et al. 1999), whereas the concentration of the boundary sediments varies between

Table 4. Cr isotopic composition for samples from the K-T boundary layer.

	$\epsilon(^{53}\text{Cr}/^{52}\text{Cr}) \pm 2\sigma$
Bidart	
Clays	-0.52 ± 0.11
Spinel crystals	-0.48 ± 0.09
Caravaca	
CAR26	-0.46 ± 0.08

The ϵ values represent the deviation of the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio from the terrestrial standard value in parts per 10^4 . The standard used in this study is a commercial Cr(III) solution for atomic absorption from Aldrich Chemical Company Inc. Data are normalized to the terrestrial $^{52}\text{Cr}/^{50}\text{Cr}$ ratio using an exponential law. The $^{53}\text{Cr}/^{52}\text{Cr}$ ratio is then renormalized to $^{54}\text{Cr}/^{52}\text{Cr} = 0$ in a similar way as Shukolyukov and Lugmair (1998). Blanks are lower than 100 pg and thus negligible.

737 ppt at Bidart and 42.4 ppb at Caravaca. It is impossible to explain the high concentration of the boundary by a mixing of sediments and volcanic rocks of mantle composition. In contrast, an addition to local sediments from a chondrite (~500–750 ppb Os) (Jochum 1996) or an iron meteorite (1–4 ppm) (Cook et al. 2004) could easily provide the high Os concentration measured at the K-T boundary (e.g., the addition of 0.11% of a chondrite for Bidart or 8.4% for Caravaca). The high Os content at the boundary is thus most likely due to an extraterrestrial input, as already proposed (Luck and Turekian 1983; Peucker-Ehrenbrink et al. 1995; Frei and Frei 2002). As Re accumulates in reducing sediments together with Os, redox conditions during deposition of the boundary clay account for the Re enrichment, with some possible loss during later oxidation at Caravaca and Stevens Klint.

Isotopic Composition

All Os isotopic ratios measured in the present study are lower than the mean $^{187}\text{Os}/^{188}\text{Os}$ ratio of the ocean at the end of the Cretaceous period (~0.39) (Ravizza and Peucker-Ehrenbrink 2003). This may be due to the input of a very high proportion of material with an $^{187}\text{Os}/^{188}\text{Os}$ ratio of about 0.12 or to diffusion and bioturbation processes that modified the signal in the sediments from above and below the boundary (Lee et al. 2003). As Re and Os can be scavenged at different rates from the water column (Ravizza et al. 2001), present-day Re/Os ratios do not necessarily reflect time-integrated Re/Os ratios that are critical for age correcting the measured Os isotope ratios. Considering the highest Re/Os obtained for one of our samples, a maximum Re-decay correction of 0.027 can be estimated for the $^{187}\text{Os}/^{188}\text{Os}$ ratio. The $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratio of the K-T boundary is higher than the ratio of all kinds of meteorites (Table 5 and Fig. 3). If the maximum Re-correction is applied, the K-T sediments are still more radiogenic than chondrites but fall in the range of iron meteorites. The $^{187}\text{Os}/^{188}\text{Os}$ ratio is also higher than that of a mantle source (0.129 for the Deccan traps) (Allègre et al. 1999). Calculations show that mixing of only 0.02 to 0.1% of

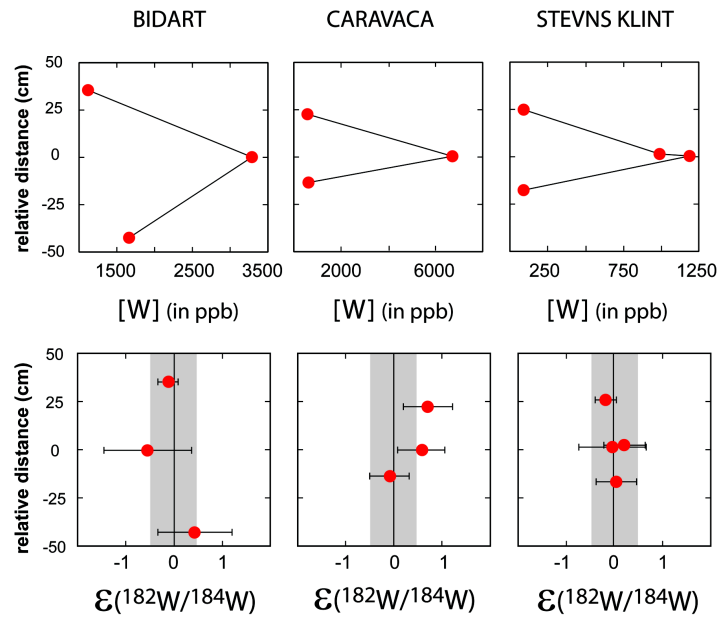


Fig. 2. Tungsten concentration and $^{182}\text{W}/^{184}\text{W}$ ratios (expressed in relative to our terrestrial standard) as a function of the distance to the K-T layer. The standard used is a commercial standard solution for inductively coupled plasma mass spectrometry (ICPMS) obtained from Johnson Matthey Co. The layer itself is strongly enriched in W but has the same isotopic composition as the surrounding sediments within uncertainty. When not shown, the error bars are smaller than the symbols. The gray band corresponds to the external reproducibility of the standard (2 σ standard deviation of replicate measurements of the standard).

Table 5. Osmium, tungsten, and chromium isotopic composition of the Deccan traps (or the silicate earth) and different types of meteorites. Literature data.

	$^{187}\text{Os}/^{188}\text{Os}$	$^{182}\text{W}/^{184}\text{W}$ (expressed as ϵ values)	$^{53}\text{Cr}/^{52}\text{Cr}$ (expressed as ϵ values)
Deccan traps	0.1288	0 (silicate earth)	0 (silicate earth)
Iron meteorites	0.121 to 0.168	-4.4 to -2.5	
Angrites		+4.6	+0.4 to +0.7
Eucrites		+2 to +39	+0.7 to +1.3
Diogenites			+0.4 to +0.6
SNC (Martian meteorites)		+0.3 to +3.3	+0.22
Ordinary chondrites (OC)	0.1286	-2 to -0.64	+0.48
Enstatite chondrites (EC)	0.1286	-2.2	+0.17
Carbonaceous chondrites (CC)	0.1258	-1.9	-0.8 to -0.3

Osmium data from Walker and Morgan (1989), Meisel et al. (1996), Smoliar et al. (1996), Birck and Allègre (1998), and Allègre et al. (1999). Tungsten data from Lee and Halliday (1997), Horan et al. (1998), Lee and Halliday (1998), Lee and Halliday (2000), Quitté et al. (2000), Kleine et al. (2002), Schönberg et al. (2002), Yin et al. (2002), Kleine et al. (2004), Foley et al. (2005), Lee (2005), and Markowski et al. (2006). Chromium data from Shukolyukov and Lugmair (1998) and Trinquier et al. (2006).

chondritic material with sediments results in our measured isotopic compositions. This is in strong contradiction to a) the 5–20% of extraterrestrial matter present in the K-T boundary according to different estimates (Alvarez et al. 1980; Kyte et al. 1980; Dia et al. 1989), and b) the results of the mixing calculation based solely on the observed concentrations (see the Enrichment in Os and Re section). In the case of an iron meteorite, richer in Os, the mass balance becomes even less favorable. Thus, no simple mixing can account for the Os data in the investigated sediments, and no definitive conclusion about the nature of the impactor can be drawn from these data.

Ni-Rich Spinel

Spinel crystals are more than 30 times richer in Os and 50 times richer in Re than sediments from the boundary itself and are characterized by a less radiogenic signature. Their $^{187}\text{Re}/^{188}\text{Os}$ ratio equals 10.3. As previously discussed, spinel is expected to carry the isotopic signature of the impactor, but all meteorites are richer in Os by a factor of at least 20 and only a few iron meteorites yield an $^{187}\text{Os}/^{188}\text{Os}$ ratio close to 0.168 (Smoliar et al. 1996; Birck and Allègre 1998). Spinel therefore does not seem to carry the intact Os signature of extraterrestrial material. The relatively high Re/Os ratio of spinel compared to values for

meteorites is probably due to a loss of Os during the formation of spinel grains, since Os is highly volatile when oxidized, and the spinel formed under high oxygen fugacity. This fractionation process has already been invoked by different authors to justify a nonchondritic Os/Ir or Ru/Ir ratio in the sediments of the K-T boundary at Caravaca (Kyte et al. 1985), in magnetic spherules in Italy (Smit and Kyte 1984), and also in numerous other sediments from the K-T boundary (Evans et al. 1993). Another possible explanation is that Os has a stronger affinity for the residual liquid phase than for the spinel whose close structure accepts only few impurities. As well as Os, the spinels are also depleted in Ir, with an Ir concentration of 22 ± 2 ppb at Caravaca, which is in good agreement with previous estimates (e.g., Bohor et al. 1986). Platinoids are probably concentrated in a residual metal phase.

When we recalculate the $^{187}\text{Os}/^{188}\text{Os}$ at the time of the impact from the high Re/Os ratio of the spinel, we find a value of 0.153. This value is higher than the isotopic composition of chondrites ($^{187}\text{Os}/^{188}\text{Os} \approx 0.129$ for enstatite and ordinary chondrites and $^{187}\text{Os}/^{188}\text{Os} \approx 0.126$ for carbonaceous chondrites) (Meisel et al. 1996) but falls in the range of iron meteorites (0.121 to 0.168). Based on the isotopic composition, the impactor may have been an iron meteorite; however, this conclusion is strongly dependent on the accuracy of the time-integrated Re correction. K-T spinel cannot form from iron meteorite material, as pure magnetite would be produced in this case. Formation of K-T spinel instead requires chondritic material (Gayraud et al. 1996). It is then likely that the Re correction is not accurate.

Tungsten

Concentrations

The sediments at the boundary contain between 1.2 and 6.7 ppm W. The W concentration in the continental crust is about 1–2 ppm (McLennan 2001), whereas it is about 0.1–0.2 ppm in chondrites (Halliday and Lee 1999) and between 0.7–3 ppm in iron meteorites (e.g., Horan et al. 1998; Markowski et al. 2006). The concentration in seawater has been estimated around 0.1 ppb (Li 1991). The W concentration of the sediments below and above the boundary at Stevns Klint and Caravaca is lower than that of the continental crust, but is the same order of magnitude as the continental crust at Bidart. If one considers a simple mixing of an exotic input with the sediments, no combination of materials can explain the high W concentrations found in the boundary sample, except possibly some iron meteorites that could be responsible for the high content in Stevns Klint. The other sites are too rich to result from a mixing between sediments and a meteorite, or even from a pure iron meteoritic component. We therefore conclude that the observed W enrichment arises from post-depositional

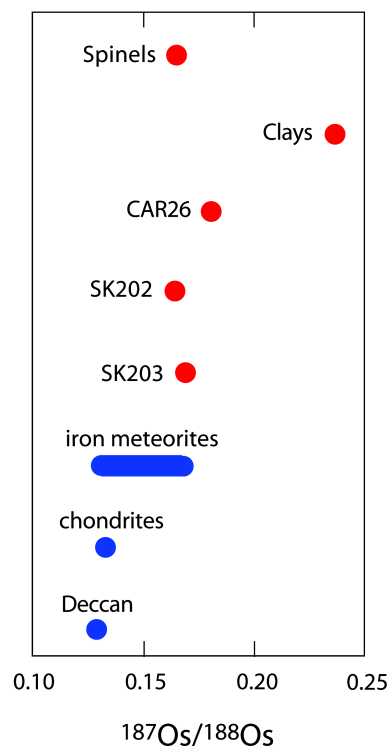


Fig. 3. Osmium isotopic composition of the studied K-T sediments and spinel, of meteorites, and of the published value for the Deccan traps. Uncertainties are smaller than the symbols. Clays and Spinel: Bidart site, CAR26: Caravaca, SK202, and SK203: Stevns Klint. The K-T samples are more radiogenic than the Deccan traps or the meteorites, except possibly the most radiogenic iron meteorites. Spinel grains are Re- and Os-rich but fractionated, so that the real isotopic composition of this phase at the time of the impact cannot be determined precisely. Meteorite and Deccan data are from Tables 2 and 5 (and references listed therein).

processes. But what mechanism could cause this observed enrichment? Lead concentration may be accounted for by scavenging of chalcophile elements at the time of sulfide precipitation (e.g., Dia et al. 1989). The carrier phases of W are not well known; it may also be trapped in sulfides, or particular redox conditions at the time of deposition may have modified its behavior in solution and favored its precipitation and deposition in the sediments. The sedimentation rate of W may also be elevated because of a diminished amount of carbonate sedimentation.

The W enrichment in the boundary layer relative to the local sediments is similar at Caravaca and Stevns Klint, but is much smaller at Bidart. The sediments surrounding the boundary at Bidart are very rich in W, probably due to W diffusion out of the boundary layer. It seems that W may have a behavior similar to that of Os, as Bidart also differs from the other sites with a small relative enrichment in Os. Indeed, W forms partially to fully de-protonated oxyacids (WO_4^{2-}) and thus has similarities to Mo, Re, and Os that are enriched in reducing sediments (Crusius et al. 1996).

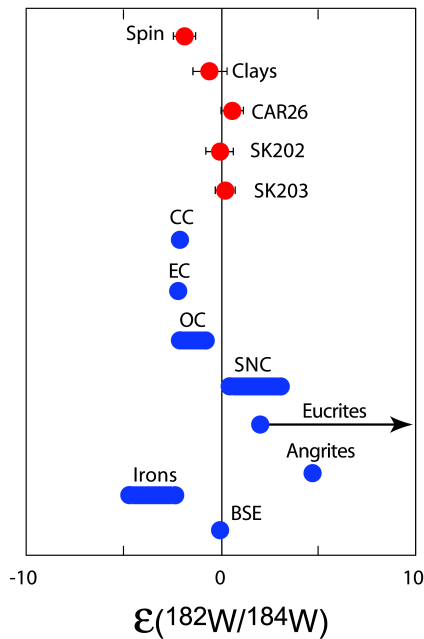


Fig. 4. Tungsten isotopic composition of sediments and spinel from the K-T boundary layer and different types of meteorites. Clays and Spin (spinel crystals): Bidart site; CAR26: Caravaca; SK202 and SK203: Stevns Klint. CC: carbonaceous chondrites; EC: enstatite chondrites; OC: ordinary chondrites; SNC: Martian meteorites; irons: iron meteorites; BSE: bulk silicate Earth. The K-T samples yield the same isotopic signature as the silicate Earth within error, suggesting mixing processes and a large contribution of terrestrial material. The isotopic composition of spinel points to a chondritic impactor. Data are from Tables 3 and 5 (and references listed there).

Isotopic Composition

The advantage of the Hf-W system is that it is based on a short-lived radionuclide, contrary to the Re-Os system. The half-life of ^{182}Hf is 8.9 Myr (Vockenhuber et al. 2004), so this isotope was already extinct 65 Ma ago and no correction due to an in situ radioactive decay is necessary. The isotopic composition has not changed since the impact; any subsequent chemical fractionation would not affect the isotopic composition. This is also the case for the Mn-Cr system.

All samples (K-T layer and surrounding sediments) present a W isotopic composition indistinguishable from the terrestrial value within uncertainties. Several interpretations are possible: either the extraterrestrial material is too diluted so that its isotopic signature is not detected, or the origin of W is terrestrial (for example coming from the Deccan traps). Another possibility is that W does originate from an extraterrestrial body, but with an isotopic composition identical to that of the Earth. However, no known meteorite has a W isotopic composition identical to that of the Earth (Table 5; Fig. 4), except possibly some ordinary chondrites (within error). However, given the W concentrations within meteorites, the W isotopic results are still in agreement with an addition to the sediments of a few percents of an iron

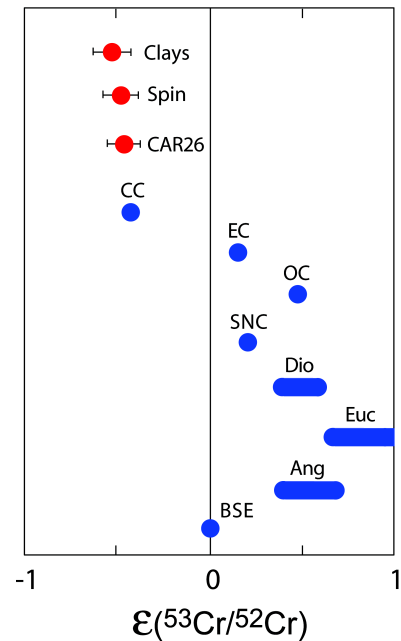


Fig. 5. Comparison of the chromium isotopic composition of K-T boundary samples with those of different types of meteorites. Clays and Spin (spinel crystals): Bidart site; CAR26: Caravaca; CC: carbonaceous chondrites; EC: enstatite chondrites; OC: ordinary chondrites; SNC: Martian meteorites; Dio: diogenites; Euc: eucrites; Ang: angrites; BSE: bulk silicate earth. The isotopic composition of the K-T layer sediments and of the spinel demonstrates that the impactor was a carbonaceous chondrite. Data are from Tables 4 and 5 (and references listed therein).

meteorite, or up to 25% of chondritic material (carbonaceous chondrite), or up to 45% of an ordinary chondrite, if future data on ordinary chondrites show an average composition at the upper end of the presently available range (see Table 5).

Ni-Rich Spinel

The mass balance is not favorable for detection of extraterrestrial W in sediments because the continental crust is highly enriched in this element. In contrast, spinel should be able to provide a strong constraint on the composition of the projectile. Spinel crystals show a deficit of $-1.7 \pm 0.5 \epsilon(^{182}\text{W}/^{184}\text{W})$. This isotopic composition is equal to that of carbonaceous chondrites, although ordinary chondrites cannot be firmly excluded because the different types of chondrites are not easily resolvable with W isotopes. The isotopic composition of spinel clearly excludes the hypothesis of an iron meteorite as the impactor (the W isotopic values for iron meteorites range indeed from -4.4 to -2.5 ; see Table 5). The W concentration of spinel is higher than chondritic, likely because this element is refractory. Volatile elements have been lost during formation of spinel resulting in an increased relative content of refractories; the chemical composition of spinel does not reflect that of the extraterrestrial material.

Chromium

We have shown that more than 95% of the Cr in the spinel is of extraterrestrial origin (see the Chromium subsection in the Results section) and clearly preserved the Cr isotopic signature of the impactor. The Cr isotopic composition of the K-T boundary samples as well as signatures for different types of meteorites and the terrestrial value are summarized in Table 5 and plotted in Fig. 5. Almost all meteorites are enriched in ^{53}Cr relative to the Earth. Only carbonaceous chondrites present a negative value for the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio relative to the terrestrial value (Rotaru et al. 1992; Shukolyukov and Lugmair 1998). This “deficit” in ^{53}Cr is only apparent in chondrites and corresponds in fact to a nucleosynthetic excess of ^{54}Cr in carbonaceous chondrites (Rotaru et al. 1992; Trinquier et al. 2006). The normalization applied for the data reduction uses the $^{54}\text{Cr}/^{52}\text{Cr}$ ratio and thus induces an apparent ^{53}Cr deficit. Only carbonaceous chondrites have the same signature as the K-T samples and the spinel crystals. This result obtained on spinel confirms that the impactor must have been a carbonaceous chondrite. The identical ratio found in bulk sediments reinforces the previous conclusions, indicating that most of the Cr present in the K-T boundary is of extraterrestrial origin (Shukolyukov and Lugmair 1998). Furthermore, the Cr concentrations and isotopic data strongly argue against the impact of an iron meteorite as these meteorites typically contain several orders of magnitude less Cr than chondrites.

CONCLUSIONS

Osmium, chromium, and tungsten concentrations in K-T boundary sediments result from a mixing of local sediments and extraterrestrial matter. Physico-chemical processes and different conditions of sedimentation depending on the site led to an enrichment of siderophile elements (Os, Re, W). The W/Os ratio in the sediments of the boundary is variable: 4452 in Bidart, 158 in Caravaca, and 76 in Stevns Klint, which indicates that the chemical fractionation varies from one site to another, depending on the processes involved and on the history of redox conditions in the sediment.

Some authors proposed that the impactor was chondritic. The Os isotopic composition and the W data for sediments are compatible with this hypothesis, even if they do not conclusively prove it. The Os isotopic composition of spinel grains agrees with an iron meteorite for the impactor, but this result is questionable because a precise time-integrated Re correction is difficult. However, W isotopes in bulk sediments definitely exclude the hypothesis that the impactor was an iron meteorite. Equally, the Cr and W isotopic analysis of Ni-rich spinel crystals can characterize the extraterrestrial bolide to be chondritic in nature. The hypothesis of a comet as the impactor, with a composition similar to carbonaceous chondrites, remains possible but lacks any experimental support.

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