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On the sodium overabundance in cometary meteoroids

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Abstract

Relative chemical abundances and physical properties of cometary meteoroids can be deduced from meteor spectroscopy. The study of moderately volatile elements like Na can provide clues on the structure of cometary particles and processes suffered by these particles. Recent studies of spectra of photographic fireballs (produced by cm-sized meteoroids) suggest that Na is enhanced in a 1.5 factor relative to the chondritic value. The observed features in the ablation of Perseid and Leonid meteoroids suggest that the particle fragmentation behavior of an important part of the large meteoroids fits well with a dustball model where Na would be associated with an interstitial material joining mineral grains. We suggest that aqueous alteration in the parent bodies of these meteoroids can promote chemical redistribution of Na as has been widely observed in carbonaceous chondrites. Then, this element is mobilised towards interstitial fine-grain materials that are joining large mineral grains. These more friable materials (rich in Na) can be ablated preferentially in the first stages of ablation. Finally, we discuss briefly the interest in the development of meteoroids.

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1. Introduction: cometary versus asteroidal meteoroids. The role of Na

The chemical composition and physical properties of meteoroids can be inferred from the spectroscopic and photometric study of their ablation columns in the atmosphere, called meteors. The flight of the meteoroid in the atmosphere produces a column of rarefied gas formed from a mixture of meteoric and atmospheric compounds, heated by the process of deceleration by continuous collisions of the incoming meteoroid with the atmospheric constituents. The kinetic energy lost produces a rise in the temperature of the meteoroid. When the temperature is higher than the evaporation temperatures of the mineral phases that form the meteoroid itself, the process known as ablation begins. Meteor spectroscopy is a valuable approach to

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the study of meteoroids because is able to provide the chemical composition and temperature characteristic of cometary particles whose size and velocity makes them unable to survive ablation. In fact, the interaction of cometary meteoroids with the atmosphere involves typically geocentric velocities greater than 25 km s^{-1} . However, high meteoric fluxes coming from lower-velocity sources have been described, such as dust trails associated with comet 21P/Giacobinni-Zinner (Simek and Pecina, 1999) or with comet Pons Winnecke (Arlt et al., 1999). The range of masses of cometary particles varies from several kg for the biggest meteoroids detected by fireball networks (Ceplecha et al., 1998) to small fragments with minimum masses of 10^{-17} g as were detected by spacecraft in the coma of comet 1P/Halley (Jessberger et al., 1988; Fomenkova et al., 1992). Due to their fluffy structure and highly volatile nature, several processes such as solar radiation, solar wind bombardment and collisions with other

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meteoroids induce a progressive alteration of these particles in the interplanetary medium. Borovička et al. (1999) reported the depletion in Na by analyzing video spectra of Leonid, Perseid and Orionid meteors. Future studies of these space-weathering processes are required because it is not yet known how efficiently meteoroids change their chemical composition during long stays in the interplanetary medium.

An important part of the Interplanetary Dust Particles (IDPs) collected in the upper terrestrial atmosphere are produced by comets. As these particles are recovered once decelerated and freely suspended in the atmosphere, all orbital information that would be derived from the geometry of its entry on their origin is lost. Despite of this some identification criteria have been developed. Under the assumption that all particles enter at 45° angle, Love and Brownlee (1994) estimated that the temperature reached by the meteoroid during atmospheric entry depends basically on its size and velocity. To reach those values they also chose a typical density of 2 g cm⁻³ that is not relevant for cometary IDPs or low-porosity asteroidal debris. Consequently, those results should be taken with caution although are a first approach to asses flash heating and deduce some general processes. For example, under Love and Brownlee (1994) assumptions, particles between one and a few tens of micrometers would be able to survive atmospheric entry for velocities between 11 and $\approx 25 \text{ km s}^{-1}$. The calculated peak temperature depending on the velocity was shown in Fig. 15 of Rietmeijer (1998) who also summarized the range of observed peak heating temperatures in collected IDPs that are essentially consistent with the theory. It is important to remark that even low-velocity particles suffer thermal alteration that affects some of the more volatile phases by inducing volatile element loss (e.g. Na, S, Zn, Se, Ge etc...) and thermal modification of Si and sulfide minerals in a process called dvnamic pyrometamorphism (Rietmeijer, 1998. 2002a,b,c). The effect of thermal modification of pyrrhotite fragments from cluster IDPs was recently described by Rietmeijer (2004). We can expect that even low-velocity meteoroids deposited in the upper atmosphere suffer thermal modification that brings them far from the original composition. These compositional changes in the surviving samples called Interplanetary Dust Particles (IDPs) have been extensively described in the literature. At $\sim 1100^{\circ}$ C the melting begins as demonstrated by studying highly vesicular IDPs (Rietmeijer, 1996). Similar features of volatile element loss are widely observed in micrometeorites (for comprehensive reviews see e.g. Rietmeijer, 1998, 2002a; Taylor et al., 2000; Flynn, 2002).

Flynn (1994) and Love and Brownlee (1994) described that the degree of heating can be derived from the amount of implanted He released by the IDPs. According this criterion, the highest peak temperatures would be experienced for high-velocity cometary meteoroids and, consequently, it was applied to distinguish between cometary and asteroidal IDPs. However, some cometary streams deliver meteoroids to the Earth under relative low geocentric velocity conditions, being the exception to the rule. Consequently, additional criteria to identify cometary IDPs are required. The slightly overabundance in Na detected by Trigo-Rodríguez et al. (2004a,b) in cometary meteoroids would be an useful criterion especially because we expect that this moderately volatile element to be depleted from asteroidal debris over long timescales by the action of space weathering (Borovička et al., 1999, 2005; Trigo-Rodríguez et al., 2004a,b). Halliday (1960) found in the spectrum of an asteroidal meteoroid entering the atmosphere at 13.4 km s⁻¹ and producing a magnitude -4.2 fireball a complete absence of D lines of Na.

2. Aqueous alteration and Na in cometary meteoroids

Meteoroids and IDPs are the disintegration products of asteroids and comets. Asteroids are quite efficiently sampled in the meteorite collections, but cometary fragments are still missing probably as consequence of the low strength of these materials, preferentially fragmented during the atmospheric entry (Campins and Swindle, 1998). From the study of cometary comae and tails we know that comets are composed of ice, organics and mineral grains. The continuous release of particles from these bodies provides the most important source of the IDPs collected in the stratosphere. Comets are expected to be unequilibrated bodies rich in water ice and other volatiles. Those volatiles under close solar proximity could be locally (preferentially inside the body) in a liquid state during appreciable periods of time but especially during the solar heating produced during their approaches to perihelion (Rietmeijer et al., 2004). Aqueous reactions promote chemical redistribution by dissolution of different elements in the fluid and ulterior precipitation (Zolensky and McSween, 1988). As a consequence, the presence of water alters mineral phases and produce phyllosilicates and other oxidized phases (Campins and Swindle, 1998; Rietmeijer et al., 2004). Under aqueous alteration Na can be easily mobilised from the original mineral phases containing this element to the interstitial material. Consequently, aqueous alteration would favour the redistribution of sodium in some volatile phases likely present in cometary meteoroids. Some authors have suggested that organics and ices are forming volatile phases preserved in cometary meteoroids (Fomenkova et al., 1992; Wooden, 2002). It is still unknown if these volatile phases are efficiently delivered by cometary IDPs to the Earth although some progress has been made recently by studying IDPs (Matrajt et al., 2003; Flynn et al., 2004). Water is also efficiently bound in phyllosilicates that are ubiquitously identified in carbonaceous chondrites that probably suffered aqueous alteration in its parent body (McSween, 1979, 1987; Tomeoka and Buseck, 1985, 1990; Browning et al., 2000).

Unfortunately, the unequivocal detection of volatile phases released from meteoroids during ablation is a tough problem. State-of-the-art remote detectors allow performing efficient spectroscopy not only in the typical panchromatic range of wavelengths, but also in the IR and UV where the release of some organic material from meteoroids can be detected. Recently, Carbary et al. (2004) reported the detection of C lines and several unidentified emission bands in the far UV (1400 to 2000 Å) part of a Leonid spectrum obtained from the Midcourse Space Experiment. In the present paper we will focus on the Na abundance in meteoroids although we will also explore the possibility that this element would be associated to other volatile phases like e.g. organics.

3. Deducing the composition of meteoroids from meteor spectroscopy

The examination of surviving IDPs has usually been made by cosmochemists through laboratory studies. However, cometary meteoroids have larger sizes than these typically surviving and are reaching the Earth preferentially at high geocentric velocities. Being fragile aggregates of dust and volatiles, we cannot expect survival of large particles if not only quenched fragments and fine dust (Rietmeijer, 2002a,c; Flynn, 2002; Padma Kumari et al., 2005). Consequently, most of the cometary meteoroids reaching the top of the atmosphere are not able to reach our laboratories. Then, meteor spectroscopy is a suitable technique to deduce the relative or absolute chemical abundances of these particles by studying the abundances in the meteor head, formed by the ablation of meteoric and atmospheric vapours.

The evolution of meteor spectroscopy was parallel to the development of photography. The first photographic program of meteors was started by Blajko in Moscow in 1904. However, the interest in meteor spectroscopy was incited by the early work of Millman who started a successful program in Canada. Halliday (1961) identified 229 emission lines in basis to five Perseid meteor spectra. This early work was followed by additional research by Cook et al. (1971), Millman et al. (1971) and Ceplecha (1973) who performed spectroscopic studies of several meteor showers. This previous work was mainly descriptive of the basic spectral features, but first attempts for deducing the chemical composition of meteors were made by Harvey (1973, 1977). A comprehensive review of the evolution of meteor spectroscopy was made by Millman (1980) and also by Borovička and Betlem (1997). Borovička (1993, 1994a) developed a physical model (based basically in the assumption of the chemical equilibrium in the meteor column) from where the chemical composition of meteoroids can be inferred. This model was applied to 15 photographic meteor spectra belonging to 13 different fireballs by Trigo-Rodriguez et al. (2003) obtaining typical chondritic compositions in the main rock-forming elements (Mg, Ca, Ti, Cr, Mn, Fe, Co and Ni). Curiously, Na exhibited an enhancement over the chondritic ratio in a factor 1.5. The Na column density in most of the analysed meteors was computed by Trigo-Rodriguez et al. (2004a) in order to demonstrate that such enhancement is seven orders of magnitude over the expected for the presence of this element in the upper atmosphere (Plane, 1991). Consequently, Trigo-Rodríguez et al. (2004a) concluded that the Na enhancement over the chondritic value is real. High Na abundances in fireballs could be characteristic of cometary meteoroids.

In the last decade meteor spectroscopy has been used to obtain information about the chemistry of cometary meteoroids and their content in volatile phases (Borovička et al., 1999: Rietmeijer and Jenniskens, 2000: Jenniskens, 2001; Rietmeijer, 2001; Jenniskens, 2004; Jenniskens et al., 2004a,b,c). A big progress has been obtained in understanding the nature of meteoric phenomenon. For example, now it is well-known that in meteor spectra, the majority of lines belong to the main spectrum characterised by a temperature of about 4500 K. However, high-velocity meteoroids also exhibit a high-temperature component reaching 10,000 K (Borovička, 1994b; Borovička and Jenniskens, 2000; Trigo-Rodríguez et al., 2003; Jenniskens et al., 2004a). The main lines associated with this second component are: H I, Ca II, Mg II and Si II. Both components must be considered in order to fit meteoric emissions, although the high temperature component weakly contributes to the spectrum of meteoroids with geocentric velocity lower than 40 km/s. For meteoroids with higher geocentric velocities, main and high temperature components are blended in the spectra. Consequently, they require a separate study as both components involve different meteoroid masses and temperatures, probably suggesting a different formation region (Borovička and Betlem, 1997).

4. Main observations on Na in cometary meteoroids

Na lines are omnipresent in cometary meteor spectra and Na abundance enhanced over the chondritic value (Trigo-Rodríguez et al., 2003, 2004a). Despite of this, Na-bearing phases are rare in aggregate and cluster IDPs and, in fact, the Na/Si ratio is typically below chondritic (Rietmeijer, 1998). The main reason is because although these particles survive entry, they are heated and consequently lost volatile elements from volatile mineral and amorphous phases. They left their Na behind when they were meteors. Also, it is important to remark that accurate quantitative electron microbeam analyses for Na are quite difficult (Rietmeijer, 1998). This would indicate that Na-rich phases are not surviving atmospheric entry of low-velocity IDP precursors (Rietmeijer, 1999) and/or that space-weathering processes are depleting the Na contained in meteoroids. We will explore the present evidence for both depletion processes in the next sections.

4.1. Na release behavior during ablation

The study of sodium lines in meteors deserves special interest for several reasons. The doublet line associated with multiplet 1 of Na I usually starts ablation before the lines of other elements. This is part for being available early in the ablation process, but also by their low excitation potential (2.1 eV) that makes possible the detection of this line even in faint video meteors (Borovička et al., 1999). These authors explained that the reason for the early apparition of the Na doublet is that the phases containing this element are probably more volatile and easy to incorporate to the vapour phase during ablation. However, from the analysis of photographic fireball spectra it has been found recently that sodium abundance along the meteoric columns is a factor 1.5 higher than the predicted from a chondritic composition (Trigo-Rodriguez et al., 2003). This finding was revisited confirming that the excess of sodium cannot be explained by the presence of atmospheric sodium, and therefore it was proposed that the overabundance could be associated with a moderately volatile reservoir (Trigo-Rodríguez et al., 2004a). During the formation of the solar system, volatile elements such as sodium were probably depleted from the inner protoplanetary disk due to intense solar radiation from the evolving Sun (Despois, 1992). Sodium abundance is expected to be higher in unprocessed bodies (i.e. comets) formed in the outer region of the disk. Consequently, it is possible that the continuous depletion and transport of Na from the inner to the outer solar system provided a continuous supply of this element to the surfaces of comets, being trapped into organics or ices. Such a scenario would support the dustball model invoked by Hawkes and Jones (1975) where Na would be associated with some volatile phase that glues mineral grains. However, probably not all meteoroids have a dustball structure as noted Murray et al. (2000) by looking the light curves of Leonid meteors. Recently, Fisher et al. (2000) proposed that the release of tiny mineral grains $(10^{-13} \text{ to } 10^{-14} \text{ g in mass})$ in Leonid meteoroids occurred at the beginning of the ablation process. We remark that it occurs at the same time that the only important line observed in meteor spectra is Na (Borovička et al., 1999; Trigo-Rodríguez et al., 2004a), suggesting that the ablation of a volatile interstitial material leave free small grains during the first stages of ablation.

As example of early appearance of the Na doublet we have selected two Perseid fireballs (PER5 and PER4) studied by Trigo-Rodriguez et al. (2003) that are shown respectively in Figs. 1 and 2. The derived Na/Si relative abundances and meteoroid masses are given in Table 1. PER4 was recorded from multiple station and, consequently, the atmospheric trajectory determined. Consequently, for this meteoroid is possible to analyse the evolution of the relative chemical abundances and temperature as function of the height (see Fig. 3). The release of Na from this meteoroid was quite uniform although a clear enhancement is noticed after the final fragmentation occurred in the segment labelled Z. However, we must remark that important differences in the Na behavior are seen from one meteoroid to another. This can be explained as consequence of heterogeneity among the meteoroids or by progressive depletion of Na during long stays in the interplanetary medium.



Fig. 1. PER5 spectrum showing the spectral wavelength and the different segments where the fireball was analysed. The meteor moved from top to bottom. The curved tracks of the background are stars produced in a non-guided exposure. In the analysis this background was subtracted. A rotating shutter cut the fireball's path in several segments. The first lines to appear belong to the Na I doublet and the N₂ band at 5893 Å and ~6350 Å, respectively. At the end of the trajectory the meteor column consists only of one Ca-rich refractory phase as deduced from the presence of only Ca lines.

4.2. On the Na depletion in the interplanetary medium

It is well known that moderately volatile elements (like Na) are depleted in the dust grains of the interstellar medium or in chondritic meteorites (Wasson, 1974; Wasson and Chou, 1974; Anders, 1975). Solar radiation and solar wind induced heating has been likely the responsible of this depletion. When we look to smaller particles like the meteoroids or IDP precursors, the depletion can be very effective. Due to their higher surface-area/volume ratio, sodium-rich phases are more easily exposed to solar radiation heating and solar wind bombardment. The depletion would be more efficient for particles altered by water as can be expected for meteoroids coming from comets (Rietmeijer et al., 2004). In fact, it is remarkable that the anhydrous IDPs are richer in volatile elements (Flynn et al., 1993). In this context, aqueous alteration would be mobilising Na outside the mineral grains in cometary bodies, and enriching the fine interstitial material. In this way, the Na present in this fine material joining the mineral grains would be easily altered by radiation during their stay in the interplanetary medium.

A clear evidence of this effect was found by Borovička et al. (1999) who observed important depletion of Na in faint Orionid meteors associated with comet 1P/Halley. They tentatively suggested that this effect would be produced by loss of Na from a thin outer layer during long stays in the interplanetary medium. They found that this effect is more important for the smallest cometary



Fig. 2. PER4 spectrum showing the spectral wavelength and the scanned segments where the fireball was analysed. The meteor moved from right to left, exhibiting several flares at the end of the trajectory. The curved tracks of the background are stars produced in a non-guided exposure. In the analysis this background was subtracted. As the imaging of the fireball from several stations was available the height along the trajectory was obtained. From those measurements Na line started at least (probably started out of the camera field) at a height of 112 km on the ground level. Mg, Si and Ca were the following lines to appear respectively at 108, 106 and 105 km. Additional profiles on the temperature along the path and the relative chemical abundance for the major rock-forming elements are given in Fig. 3.

Table 1

Na/Si relative abundance and mass for 5 Perseids (PER) and one Leonid (LEO) analysed in Trigo-Rodríguez et al. (2003)

Spectrum	Na/Si	Mass (g)	Diameter (mm)	
			$\rho = 1.0$	$\rho = 0.1$
PER1	0.08 ± 0.02	0.2	7	16
PER2	0.04 ± 0.02	1 ± 0.5	12	27
PER3	0.08 ± 0.03	4 ± 1	20	42
PER5	0.07 ± 0.04	6 ± 4	23	49
PER4	0.11 ± 0.02	29 ± 17	38	82
LEO	0.08 ± 0.02	250 ± 90	78	168

The mass was calculated there as a first approach as estimated from maximum magnitude of the meteors by using Verniani (1973) equation. For PER2 was only analysed the ending flare of the meteor while for the rest of the meteors the Na abundance was averaged on several segments along the meteor path. An approximate diameter (only for comparison purposes) is given assuming spherical shapes and likely meteoroid densities (in g/cm³).

meteoroids, those that produce faint meteors usually only accessible to study by video techniques. This effect might be not so important for larger meteoroids as those typically producing photographic fireballs. In fact, the Perseid photographic sample analysed by Trigo-Rodríguez et al. (2003) is characterised by particles in a range of one millimetre to several centimetres (Table 1) where the volatile content is probably preserved inside. Fig. 4 shows that these particles have similar Fe/Si than chondritic meteorites or 1P/Halley dust, but a clear enhancement in Na.

Recent models that derived the orbital elements, positions and release ages of Leonid dust trails (Asher, 1999; Lyytinen and Van Flandern, 2000; Lyytinen et al., 2001) can be also applied to other streams (Lyytinen and Jenniskens, 2003). By knowing the release ages of the meteoroids forming a dust train, we will have the chance to test the progressive Na-depletion as function of the exposure time to the interplanetary medium (Rietmeijer, 2002b). In fact, photographic multiple-station techniques confirm that dust trails bring young meteoroids to the Earth's vicinity with orbital elements that are distinguishable from the annual component (Betlem et al., 2000; Trigo-Rodríguez et al., 2002, 2004a).

5. Future work: detection of organics and molecular bands

Advances in the knowledge of the interaction of volatiles with the terrestrial atmosphere involve the use of CCD cameras and high-resolution video systems sensitive to UV and IR bands of the electromagnetic spectrum. In meteor columns in the visual range, N₂, FeO and probably other oxides as MgO (Borovička and Betlem, 1997) are often detected. In photographic meteor spectra of Perseid fireballs the nitrogen molecular band is usually present at high altitude. For example, in the PER4 fireball, the first indications of N₂ radiation start at 110 km (Fig. 1). This band is diffuse and clearly defined from the Si II line (see e.g. Fig. 5). The main contribution to this band is atmospheric because in the middle atmosphere molecular nitrogen is particularly stable since it cannot be photodissociated below the mesopause (Brasseur and Solomon, 1986).

The detection of organic matter in meteors continues to be elusive although the application of high-resolution CCD spectroscopy of air plasma emissions and a better theoretical knowledge of the associated chemistry in these hightemperature rarefied flow conditions have offered the first clues (Jenniskens et al., 2004a). Application of IR techniques to study organic mid-IR vibration bands may be challenging in obtaining direct information on the survival of volatiles and organic matter in meteoric columns. The ideal wavelength range to be covered by a generic instrument would be in the range of 1 to 20 μ m with a resolution between 0.1 and 0.01 μ m in order to register the emission and absorption bands of the principal expected volatiles. Pioneer work in the detection of meteors in mid-IR is



Fig. 3. Temperature of the main component and relative chemical abundances deduced as a function of meteor height for the lower part of the PER4 spectrum.



Fig. 4. Plot of Fe/Si versus Na/Si ratios deduced for cometary meteoroids (Trigo-Rodríguez et al., 2003). PER#=Perseids, AND=Andromedid and LEO=Leonid. Please note that the Na/Si ratio for IDPs represents a lower limit because probably Na-bearing phases are invariably lost during flash heating (see e.g. Rietmeijer, 1999). All particles show nearly chondritic Fe/Si ratios, but they show a clear enhancement in Na/Si.



Fig. 5. Segment C of the analysed PER3 fireball. Surrounding the Si II-2 line is the contribution of $N_{\rm 2}$ band.

relatively recent and was made during the 1998 Leonid Multi-instrument Aircraft Campaign (Leonid MAC) (Rossano et al., 2000). One year later, the first mid-IR spectra of persistent trains with probable identification of CH_4 , CO, CO_2 and H_2O species were obtained from the 1999 Leonid MAC (Russell et al., 2000). Although these authors proposed the condensation of such volatiles after the pass of the meteor when the temperature in the gaseous column was about 300 K, recent observations (Jenniskens et al., 2004c) propose that some of these molecules (or even large organic compounds) could survive to the ablation phase. As an additional evidence of the presence of carbon-bearing species, the detection of carbon lines has been also reported in a far UV Leonid spectrum (Carbary et al.,

2004). Also, additional simultaneous observations in the range of 780–840 nm can provide information on the presence of the OH Meinel band that has been recently proposed as linked to the presence of water in meteoroids (Jenniskens et al., 2004b). The survival of organics to meteor ablation would have important implications into the enrichment of the Earth previous to the apparition of life (Jenniskens et al., 2000).

6. Conclusions

Remote studies of meteors provide valuable data on the chemical composition and properties of meteoroids. The study of moderately volatile elements like Na in meteor spectra can provide important clues on the chemistry of cometary matter and its chemical evolution under thermal and aqueous processing. From the present review, we conclude the following:

- (i) As Na is easily detected remotely, it could be used as a tracer of the volatile phases associated with a cometary origin. The observed depletion in Na for small meteoroids as function of the time exposure to solar radiation predicts that asteroidal debris will be Napoor materials.
- (ii) Emerging research on meteor spectroscopy can bring new clues on the space weathering processes suffered by cometary meteoroids. Meteoroids with high surface-area/volume ratios are expected to suffer a higher depletion of Na and other volatile phases through solar radiation heating. This effect seems to be time dependent, being more intense for the oldest meteoroids, as e.g. those of sporadic origin.
- (iii) The Na enhancement measured in fireball columns associated with cometary meteoroids (Trigo-Rodríguez et al., 2003, 2004a) suggest a Na higher abundance than chondritic for comets. The ablation behavior suggests that the extra Na required would be forming part of an interstitial material joining mineral grains. Our picture favours the dustball model of Hawkes and Jones (1975).
- (iv) Although Na is practically omnipresent in cometary meteor spectra, Na-bearing phases are rare in aggregate and cluster Interplanetary Dust Particles (IDPs), where the Na/Si ratio is usually below the chondritic value (Rietmeijer, 1998). It suggests that cometary IDPs suffer Na depletion in their atmospheric entry and/or in the interplanetary space.

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