

Quantification of the Abrasive Wear of a Gold Wedding Ring*

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Abstract

Pieces of gold jewellery, especially rings, are known to suffer continuous abrasion during the time they are worn. This fact causes troubles in chemical analyses, because analytical methods that are sensitive in the determination of gold, especially Neutron Activation Analysis (NAA), are often faced with contamination of gold from human fingers. Since no other piece of jewellery is worn more often and regularly than wedding rings, quantification of the abrasion of a wedding ring is necessary. In this study, the abrasion of an 18 carat gold wedding ring was quantified by weighing the ring weekly over the period of one year. The composition of the ring (75 Au – 15 Ag – 10 Cu) was determined using NAA. In one year, the ring lost 6.15 mg (0.39 mm³) 18 carat gold due to abrasive wear. The highest abrasion could be observed in the course of vacation on the beach, where obviously the friction with sand increased the abrasion. Gardening and skiing also result in increased abrasive wear. However, the author suggests not wearing rings in analytical laboratories to avoid this contamination.

Keywords

Gold jewellery, jeweler, contamination, abrasion, corrosion, neutron activation analysis.

* Dedicated to my wife Veronika Steinhauser on the occasion of our first wedding anniversary.

Introduction

Gold pieces of jewellery are known to continuously abrade during the time they are worn. Rings are the most affected type of jewellery in this respect due to increased mechanical stress in the course of any manual work. Jewellers are therefore faced with the problems of destructive wear on gold pieces of jewellery in their everyday work. On this account, research on gold alloys with increased hardness and wear-resistance for use in jewellery has been a challenge for metallurgists for a long time; see, for example, Refs. [1-4]. Also, many scientists focus their work on the wear mechanisms of (precious) metals and alloys, see, e.g., Refs. [1; 4-7].

Due to abrasion of metal particles, human fingers wearing gold rings leave a trace of gold almost everywhere. The work of Gwozdz and Grass [8] showed that many artefacts touched by hand can contain gold that definitely does not come from the production. Typical examples for gold-contaminated everyday-objects are handholds, coins, handrails, steering-wheels, cutlery and so on. Of course, most of the metal is abraded by the skin [8-10]. Sometimes the abrasion of metal particles of gold jewellery even causes the appearance of black marks on the skin. This phenomenon is called “black dermographism” [11].

As a consequence of the abrasive wear, gold can be found in street and house dust (with a very high enrichment factor compared with soil) [12] and even in laundry drier lint [13]. Toelg [14] reported on this in the course of the production of ultrapure water, finding he was unable to remove impurities of approximately 100 ppt silver and gold.

Wedding rings play an important role as a source of contamination, because they are often worn regularly, and during most of everyday life, including work. Thus they are regarded as a status symbol of their owner rather than just a piece of jewellery.

Apart from the loss of material and scratches on the ring's surface, the wear becomes problematic when analytical samples or analytical laboratories are contaminated with gold. Analytical methods that are sensitive in the determination



Figure 1

The author's wedding ring

of gold, primarily Neutron Activation Analysis (NAA), are therefore sometimes faced with gold contamination caused by the abrasive wear of rings. Gwodziński and Grass [8] showed that intentional rubbing of a gold ring on a quartz microfibre laboratory filter causes an abrasion of up to 0.37 µg gold. This scenario is a good basis for further investigations, but since the abrasion in this experiment was performed on purpose, it is not suited to simulate the loss of material over a long time by everyday stress and friction. Thus the determination of the wear rate of a gold ring in everyday use and its dependency to various factors, e.g. manual activity, were the topic of this study.

Radiochemical background

NAA is an excellent analytical tool for qualitative and quantitative analysis of a number of elements [15]. The principle of this method is the following: The sample is exposed to the neutron beam of a neutron source (preferably a research reactor). Upon neutron capture, a very small, but representative part of the nuclei in the sample is activated. The γ -photons emitted upon decay of those artificial radionuclides is then measured with a γ -photon-detector [16].

Gold offers excellent properties for NAA (see also [17]):

- 1 Gold consists of only one stable nuclide: ^{197}Au
- 2 The cross section for neutron capture of thermal neutrons, following the nuclear reaction $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$, is $\sigma = 98.659\text{ b}$ ($1\text{ barn} \equiv 10^{-24}\text{ cm}^2$), which is much larger than the cross section values of most other stable nuclei.
- 3 The half-life of the activation product ^{198}Au is 2.6956 d, which is very suitable, because it is short-lived enough, to obtain a high specific activity in the gold containing sample, even after a short irradiation time in the reactor. On the other hand, its half-life is long enough for cooling of disturbing matrix elements (like Al, Cu, Ag), and many others), which allows easy and safe handling. Nevertheless, the half-life of ^{198}Au is short enough to allow cooling of an activated sample with a high gold-content for an undisturbed measurement and determination of other, long-lived radionuclides (like, for example, ^{60}Co , ^{59}Fe , ^{65}Zn , ^{192}Ir and many others).
- 4 Upon disintegration, ^{198}Au emits γ -photons with an energy of 411.80205 keV and a branching ratio of 95.98%. This γ -radiation causes an almost undisturbed photo-peak in the γ -spectrum. Moreover, modern semiconductor detectors (like High Purity Germanium, HPGe-detectors) show a good detection efficiency for photons with this energy.

All these features listed above and the fact that the nuclear properties of ^{198}Au are well-known from experiments and calculations make gold the most frequently used neutron flux density monitor for neutron sources.

In summary, gold can be determined by NAA with extreme sensitivity. After one week of irradiation at a thermal neutron

flux density of $10^{14}\text{ cm}^{-2}\text{s}^{-1}$, the detection limit is $10^{-13} - 10^{-12}\text{ g}$ per 1 g of sample [18]. Only two elements of the periodic table (dysprosium and europium) can be determined with significantly higher sensitivity using NAA under these optimised conditions.

Instrumental Neutron Activation Analysis (INAA) is generally not able to differentiate between the chemical characteristics like the oxidation state or the chemical bonds of the element that is determined in a sample. Thus there is no possibility for INAA for chemical speciation and differentiation whether a sample, e.g. containing Au(I) or Au(III) compounds may be contaminated with metallic gold particles. In general, one main methodological advantage of INAA compared to other analytical methods is a simple and straightforward sample preparation: The aliquot that is analysed only has to be representative for the whole amount of sample material. Homogeneity is therefore a prerequisite. Unfortunately, the procedure of homogenisation is not only time-consuming but also offers the possibility for the analytical chemist to run the risk of contamination, if homogenisation is performed manually. Geological samples, for example, can be homogenised by grinding in an agate mortar [15]. Mechanical stress on the agate pestle and friction may increase the abrasion of a gold ring that is worn during this procedure.

To avoid the problems with homogenisation, activation of large samples is a suitable alternative. Many research reactors offer the possibility for activation of samples of 1 kg or more, which helps keep homogenisation to a minimum. This strategy is of course not advisable in every analytical case.

Unless otherwise noted, all nuclear data in this paper were taken from the National Nuclear Data Center [19].

Materials and methods

Material

The author's wedding ring has been the object of investigation. It is a plain ring made of 18 carat yellow gold, with an inner perimeter of 58 mm, a width of 3.90 mm, a maximum thickness of 1.77 mm, an initial weight of 5.58387g and a Vickers hardness of approximately 135 HV. It is engraved on the inner side with a hallmark and "750" (symbol for 18 carat) and the words "Veri 1. Juli 2006", as shown in Fig.1. The author wears it on the ring finger of the right hand, which is an Austrian tradition. The author is also right handed. In Vienna (from July to December 2006), the author spent approximately 25% of his working time in the laboratory and 75% in his office (with large variations), in Munich (from January to July 2007), the ratio was approximately 75:25.

Weighing

Weighing was chosen to be the method of choice for the objective of this study. The ring was weighed once weekly (Thursday, if possible), over the period of one year, beginning one week after the wedding ceremony. The microanalytical balances were a Sartorius Research™ (property of the

Table 1

Summary of the nuclear properties of the activation products of copper, silver, iridium and gold that are essential for NAA

Element	Activation product	Half-life	γ -photon energy (keV)
Cu	^{66}Cu	5.120 min	1039.2
Ag	^{108}Ag	2.37 min	632.98
Ir	^{192}Ir	73.827 d	316.50618
Au	^{198}Au	2.6956 d	411.80205

Atominstitut in Vienna) from July 2006 to January 2007 and a Mettler Toledo AT261 DeltaRange™ (property of the LMU Munich) from January to July 2007. Extraordinary events like unusual manual work, vacation, or hot or cold weather were noted. These events might have led to unusually high or low abrasion. The ring was worn every day, but only during the daytime (approximately 16 hours per day), avoiding abrasion by friction with the sheets.

To guarantee comparable conditions and to remove superficial contaminations like fat or soap, the wedding ring was thoroughly washed with distilled water and acetone in an ultrasonic bath (duration approximately 60 s each) and air-dried before weighing. Weighing was performed three times each, and in every weighing cycle the author waited for at least 60 s to guarantee complete stabilisation of the balance. To make sure that the washing procedure in the ultrasonic bath did not cause additional wear that could have been misattributed to the “natural” abrasion during the time of wearing, the whole washing procedure was repeated once immediately after a weighing cycle. The results of the second weighing cycle were identical with those of the first cycle, showing that the method was suitable for this study.

In addition to the weighing, the ring's thickness was determined in December 2006 and June 2007 with a digital vernier micrometer.

Neutron Activation Analysis

The composition of the wedding ring was determined using Neutron Activation Analysis. The nuclear properties of the elements forming the most common alloys used for rings are listed in Table 1.

In order not to destroy the author's wedding ring for this analysis, a ring from the same production batch was sampled and analysed. This ring was a donation by Juwelier Anton Heldwein, 1010 Wien, Austria.

INAA

In a preliminary experiment, the author applied INAA for the determination of the ring's major constituents, but this plan failed. In this experiment, three samples of 2 to 11 mg were cut off the ring and activated as a whole; a gold foil was used as a standard for the quantification of gold. Although the ring has a certified gold content of 750‰, this experiment produced large variations and false results of 70% Au (lowest sample mass) to 40% Au (highest sample mass). Obviously,

the neutron flux inside the thick, nugget-like sample had been significantly decreased by self-absorption of the sample. Moreover, γ -ray self-attenuation of the bulk gold sample is a likely explanation of this phenomenon. The half-value thickness for the 411.8 keV γ -ray in gold is 1.75 mm [20]. Both phenomena can occur in samples, whose matrices consist of nuclides with a high cross section for neutron capture and with high density materials, see, for example, Ref. [8]. Both are true for the wedding ring sample. To overcome this problem, a variation on Radiochemical Neutron Activation Analysis (RNAA) was necessary to determine the sample composition. However, for qualitative determination of trace impurities in the material, activation of the gold grain as a whole was applied (qualitative INAA).

RNAA

From the problems described above, it is obvious that reliable results can only be obtained by activation of a diluted solution. Thus, sample preparation was performed as follows: A piece of 5.5 mg was cut off the ring using a wire cutter, washed in 30% hot HNO_3 (65% Merck™, Darmstadt, p.a.) to remove any particles from the wire cutter and dissolved in a few ml of boiling aqua regia (1 part HNO_3 , 3 parts 37% HCl, Riedel de Haën™, Seelze, p.a.). To avoid boiling retardation, a few small grains of SiO_2 (Merck™, Darmstadt, p.a.) were added to the flask. After the reaction had stopped, the excess of aqua regia was partly evaporated (not to complete dryness), in order to avoid an unnecessary high ^{38}Cl background as a consequence of the activation of the chloride present in excess. The residual acid was carefully neutralised using an ammonia solution (25% Merck™, Darmstadt, suprapur™). With an excess of ammonia, solid silver chloride on the bottom of the flask dissolved as a $[\text{Ag}(\text{NH}_3)_2]^+$ - complex, and the solution turned blue due to the formation of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ - complex. For stabilisation, 78 mg of potassium cyanide (Merck™, Darmstadt, p.a.) were added to the solution. This leads to the formation of stable cyano-complexes and prevents the precipitation of potentially hazardous explosive substances, like silver amide (AgNH_2) or silver nitride (Ag_3N) or a mixture of incompletely defined nor characterised gold(III) amides, imides, amines, chlorides, hydroxides and oxides generally known as “fulminating gold” [21–25]. Upon addition of potassium cyanide, the solution lost its colour immediately, and the flask was filled with water to 100 ml. Aliquots of 200 μl were pipetted into polyethylene irradiation-vials. For

Table 2

Thickness of the ring in mm, measured in three different positions

	Position of the measurement		
	On the “V” of the engraved word “Veri”	Between the hallmark and the word “Veri”	On the opposite side of the word “Veri”
December 2006	1.75	1.75	1.77
June 2007	1.74	1.74	1.76

quantification, the following single element standards were used: gold-foil (high purity neutron flux density monitor-grade, used at the Atominstitut), dissolved in aqua regia; silver nitrate (Merck™, Darmstadt, p.a.), dissolved in diluted HNO₃; and a copper standard solution (Kupfer-Standardlösung gebrauchsfertig, Merck™, Darmstadt).

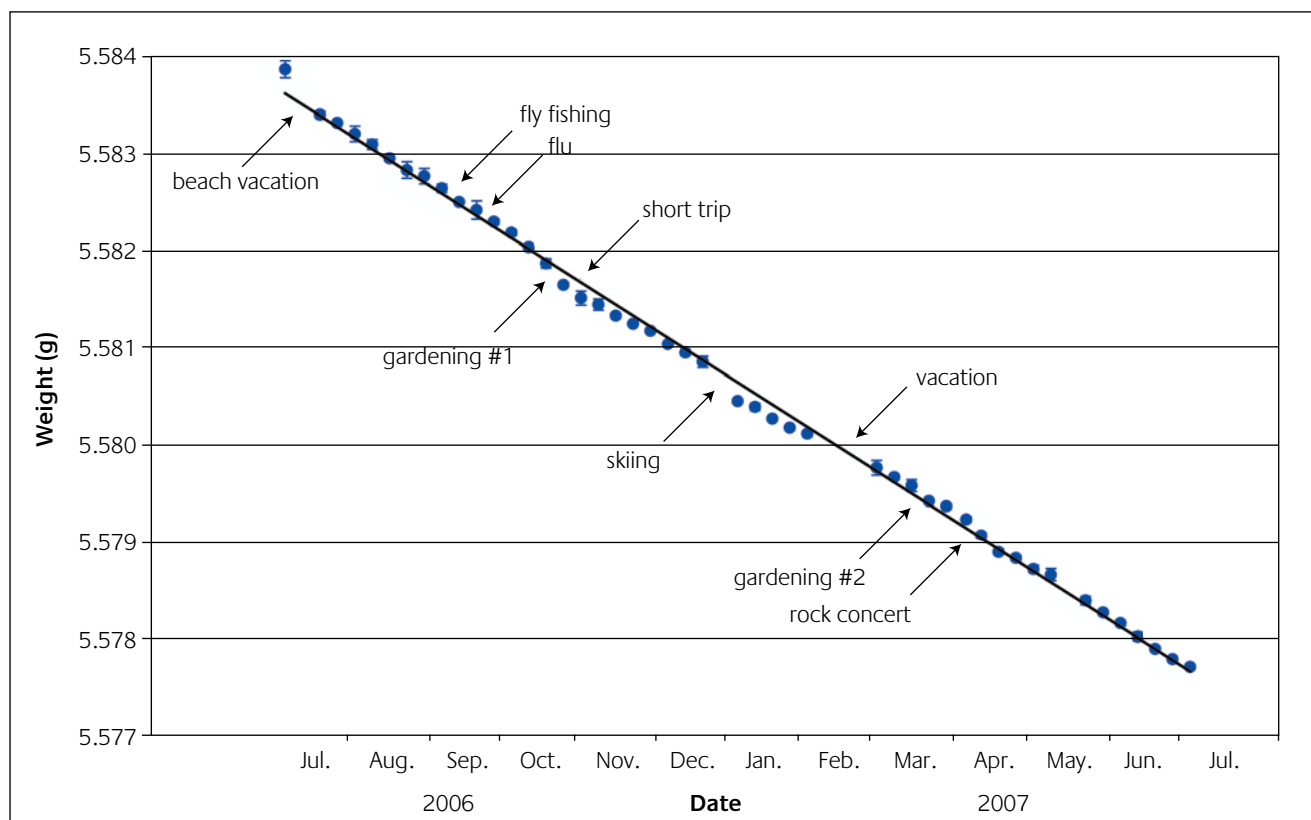
Both standards and sample solutions were irradiated sequentially using the pneumatic sample transfer system of the TRIGA Mark II research reactor at the Atominstitut in Vienna. The thermal neutron flux density in this position is approximately $3 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Irradiation time was 60 s, the measurement started after a cooling time of approximately 200 s and lasted for 300 s. All samples were measured in a fixed position at a distance of 4 cm beside the detector. The γ -spectrometry was performed with a 222 cm³ HPGe-detector (1.78 keV resolution at the 1332 keV ⁶⁰Co peak; 48.2% relative efficiency), connected to a PC-based multi-channel analyser with a preloaded filter and a Loss-Free Counting system. For qualitative determination of any long-lived activation products (for example ¹⁹²Ir), a piece was cut off the ring and irradiated

for 20 min. Measurement was started after a cooling time of 41 d in this case.

Results and discussion

The composition of the author's wedding ring, as determined by RNAA, is $74.5 \pm 1.2\%$ Au, $14.8 \pm 0.4\%$ Ag, and $9.6 \pm 0.8\%$ Cu (weight per cent). This is close to the standard pale yellow (75 Au – 16 Ag – 9 Cu), designated 2N alloy. Additionally, traces of iridium were determined by INAA (less than 1‰ per weight Ir). Obviously, iridium is added in traces to the alloy either to increase its hardness and improve its resistance to wear [26, 27] or, in this case more likely, to act as a grain refiner [2, 3].

In six months, the ring's thickness is reduced by approximately 0.01 mm (see Table 2). The results of the weighing are presented in Fig 2. Error bars shown there are for the confidence interval $P = 95.00\%$. Over the period of one year, the ring lost 6.15 mg of 18 carat gold. The average weekly abrasion is therefore 0.12 mg. This is in good agreement with an early

**Figure 2**

The ring's loss of weight over the period of one year. Extraordinary events (potentially) influencing the abrasion are noted for a certain date

Table 3*Abrasive wear over the year*

...month		The ring's abrasion (in mg 18 carat gold) per...	
		...meteorological season	...half-year
July 2006	0.61	Summer (including June 2007)	1.60
August 2006	0.48		
September 2006	0.50		author in Vienna 3.41
October 2006	0.63	Autumn	1.59
November 2006	0.46		
December 2006	0.60		
January 2007	0.44	Winter	1.39
February 2007	0.35		
March 2007	0.45		author in Munich 2.73
April 2007	0.56	Spring	1.50
May 2007	0.50		
June 2007	0.50		

Table 4*Some unusual events and their effect on the abrasive wear compared to the average weekly abrasion: 0.12 mg*

Event	Weekly abrasion (mg)	Event	Weekly abrasion (mg)
Vacation on a sandy beach	0.23	Skiing	0.20
Fly fishing	0.14	Three weeks vacation (no sand)	0.09
Two days in bed (flu)	0.12	Gardening (#2)	0.16
Gardening (#1)	0.22	Rock concert (clapping hands)	0.17
Short trip (heavy suitcase)	0.14		

study by Taylor [28, 29], who compared the wear rate of 14 and 18 carat rings. For 18 carat rings, he found weight losses between 8 mg and 70 mg.

In addition to abrasive wear, corrosion and partial dissolution of the alloy may contribute to the loss of weight [1]. However, especially for sweat-induced corrosion, for two reasons it can be assumed that this corrosion is of much less importance than the mechanical wear: Firstly because of the noble character of the ring's alloy and secondly, because no significant temperature-dependence (and thus sweat-dependence) in the loss of weight could be observed. Table 3 shows the overall loss of weight per month, meteorological season and half-year over the period of investigation. The hypothesis that sweat-induced corrosion contributes only marginally to the total loss of weight is supported by the results of a simple experiment in the course of this study: The ring was treated in 10 ml of a solution of "artificial sweat" for two days. The solution (pH = 6.0) was prepared of 275 ml water, 0.58 g sodium acetate, 0.38 g isoleucine, 0.34 g sodium chloride, 0.18 g potassium chloride and 0.17 g lactic acid, according to the average composition of human sweat [30]. The solution was analyzed by ICP-AES and did not trace any dissolved gold. This observation is also in good agreement with Taylor [29].

Vacation on the sandy beaches of Gozo (Malta) significantly increases the loss of weight: obviously the sand acts as an

abrasive on the metal surface. Another explanation for this extreme abrasion could be that the author had never worn a ring until his wedding one week before and he had to get used to the ring on his finger and not to hit and scratch it in any possible occasion. Other unusual events like gardening, skiing (wearing of gloves!) or attending a rock concert (probably due to continuous hand clapping), show slightly increased abrasion in the following weighing cycles (see Table 4). Although the author's job is not a hard manual labour, it seems to cause a higher abrasion than a three week holiday in Australia and Oceania (in February 2007; no sandy beaches). Being ill and spending two days of the week in bed does not show a significant difference in the abrasion, neither does fly fishing with a cork handled rod, nor travelling in the course of a short trip to Madrid (despite carrying a heavy suitcase).

Interestingly, each event causing an unusually high abrasion was often followed by weeks of lesser loss of weight, as shown in Figure 2 (especially after gardening). The author has no explanation for this phenomenon, it may just be coincidence. However, the ring's abrasive wear rate is almost linear over the year (coefficient of determination $R^2 = 0.9979$; regression line $y = -2 \cdot 10^{-5} x + 6.2186$). The ring's density is 15.57 g/cm^3 [31]. Thus the total volume of abraded material from the ring is 0.39 mm^3 .

Provided continuous abrasion over the day, the author “contaminated” his lab(s) in estimated 1040 hours of laboratory-working with approximately 1 mg of 18 carat gold. In the future, the author will take off his ring in the analytical lab and advise his co-workers to join him.

It can be assumed that a squiggled or ornamented ring increases wear. Also, more than one ring per finger or rings in direct contact to each other as well as hard manual labour may cause a much higher abrasion, as shown by Taylor [28, 29]. From this point of view, the ring’s abrasive wear rate presented and discussed in this study can be regarded as the minimum. Many ring owners face much higher wear due to the above mentioned factors and need more than one wedding ring over their lifetime, because of wear-induced failure after several years. However, the author’s wedding ring will become thinner and probably the engraving will disappear after some years of wearing.

Conclusions

The abrasive wear of a gold wedding ring causes continuous, almost linear loss of weight (in the first year). The total loss of material was found to be 6.15 mg (0.39 mm³) of 18 carat gold. The abrasive wear does not show a significant dependency to the season or outside temperature, but very much to the owner’s physical activity: wearing of the ring during hard manual labour or during sports or on a sandy beach increases the abrasion to a large extent. Weight losses caused by sweat corrosion can be neglected compared with abrasive wear.

The author strongly suggests to not wear gold rings in analytical laboratories that are dedicated to the analysis of traces of metals, because a gold ring or the skin that has been in contact with the ring are possible sources of contamination. Surface analytical methods like Secondary Ion Mass Spectrometry (SIMS), X-Ray Fluorescence (XRF) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) might be even more affected by such contaminations than bulk analyzing methods like NAA.

In Vienna, a city of some 1.7 million inhabitants, there are approximately 307 000 married couples [32]. Assuming that approximately 60% of them wear a wedding ring (made of 18 carat gold) regularly, the abrasion of 368 400 wedding rings would cause the annual total loss of 2.2 kg 18 carat gold with a value of approximately 35 000 € (assumption: 16 € per g).

This study also demonstrates the excellent suitability of Neutron Activation Analysis for samples containing precious metals (especially gold). The Atominstitut is open for collaboration in any scientific and industrial field, where NAA might help solve a problem – especially for the determination of trace amounts of gold in potentially critical matrices, where, for NAA, probably only a minimum of sample preparation is deemed necessary.

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About the author



Dr. Georg Steinhauser is a new member of the gold-enthusiastic community. He works in several disciplines of radiochemistry and inorganic chemistry. Currently, he serves as a post-doctoral fellow at the LMU in Munich in the field of energetic materials (with financial support of the Erwin Schrödinger Auslandsstipendium of the Austrian Science Fund, project No. J-2645-N17).

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