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Bromine Isotope Variations in Magmatic and Hydrothermal Sodalite and Tugtupite and the Estimation of Br Isotope Fractionation between Melt and Sodalite

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Abstract: We determined the bromine isotope compositions of magmatic and hydrothermal sodalite (Na₈Al₆Si₆O₂₄Cl₂) and tugtupite (Na₈Al₂Be₂Si₈O₂₄Cl₂) from the Ilímaussaq intrusion in South Greenland, in order to constrain the Br isotope composition of the melt and hydrothermal fluids from which these minerals were formed. Early formed magmatic sodalite has high Br contents $(138 \pm 10 \ \mu g/g, n = 5)$ and low δ^{81} Br values (+0.23 $\pm 0.07\%$). Late stage hydrothermal sodalite has lower Br contents (53 \pm 10 µg/g, n = 5) and higher δ^{81} Br values (+0.36 \pm 0.08‰). Tugtupite that forms at even later stages shows the lowest Br contents ($26 \pm 2 \mu g/g$, n = 2) and the highest δ^{81} Br values (+0.71 \pm 0.17‰). One hydrothermal sodalite has a Br concentration of 48 \pm 9 µg/g and an exceptionally high δ^{81} Br of 0.82 \pm 0.12‰, very similar to the δ^{81} Br of tugtupites. We suggest that this may be a very late stage sodalite that possibly formed under Be deficient conditions. The data set suggests that sodalite crystallises with a negative Br isotope fractionation factor, which means that the sodalite has a more negative δ^{81} Br than the melt, of -0.3 to -0.4% from the melt. This leads to a value of +0.5 to +0.6% relative to SMOB for the melt from which sodalite crystallises. This value is similar to a recently published δ^{81} Br value of +0.7% for very deep geothermal fluids with very high R/Ra He isotope ratios, presumably derived from the mantle. During crystallisation of later stage hydrothermal sodalite and the Be mineral tugtupite, δ^{81} Br of the residual fluids (both melt and hydrothermal fluid) increases as light ⁷⁹Br crystallises in the sodalite and tugtupite. This results in increasing δ^{81} Br values of later stage minerals that crystallise with comparable fractionation factors from a fluid with increasingly higher δ^{81} Br values.

Keywords: bromine isotopes; sodalite; tugtupite; isotope fractionation

1. Introduction

Since the development of techniques to measure stable bromine (Br) isotopes in geological systems [1], our knowledge on Br isotope systematics has increased significantly. Our knowledge is currently mostly restricted to aqueous systems and salt deposits and to some environmentally relevant organobromine systems that are Br-rich, and where Br can easily be extracted in sufficient quantities for isotope analyses [2]. Depending on the analytical technique either about 1 mg (isotope ratio mass spectrometry (IRMS) [1,3]) or 25 μ g (multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [4,5]) of Br is necessary for a reliable measurement. The large amount of Br necessary for isotope analysis has, until now, prevented the measurement of Br isotopes in rock samples.

Bromine has two stable isotopes, ⁷⁹Br and ⁸¹Br, which are about equally abundant. Variations in the ratio of these isotopes are reported as δ^{81} Br which is defined as [6]:

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \tag{1}$$



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In this equation, δ stands for δ^{81} Br, R_{sample} for the 81 Br/ 79 Br ratio of the unknown sample, and $R_{standard}$ for the 81 Br/ 79 Br ratio of the international reference standard. In the case of Br, the international reference standard is ocean bromide, abbreviated as standard mean oceanic bromide (SMOB). The oceans are a well-mixed reservoir of bromide and it has been shown [7] that isotope variations between samples taken from various locations are less than the error of measurement as is the case for Cl [8], where the international standard is ocean chloride, abbreviated as standard mean oceanic chloride (SMOC) [9].

Bromine isotope variations in groundwater and evaporite samples suggest that they are relatively small. Data published prior to 2014 showed that most δ^{81} Br values are between -0.5 and +2.0% [2] and more recent studies extended that range to between -1.5 and +3.35% [10].

In a recent study, an attempt was made to estimate both the Cl and the Br isotope composition of the mantle [11]. Based on the ${}^{3}\text{He}/{}^{4}\text{He}$ ratios of geothermal water from Mexico, Pinti et al. [11] selected samples with a mantle origin (highest ${}^{3}\text{He}/{}^{4}\text{He}$) and observed relatively high δ^{37} Cl and δ^{81} Br values in these geothermal waters. Their conclusion, based on an observed R/Ra of about 8 for the most 3 He rich samples, was that both Br and Cl isotope values of the upper (depleted) mantle are relatively heavy with respect to modern ocean bromide and chloride at +0.7-+0.9%. For Cl, this value is higher than previous estimations based on measurements of Cl isotopes in Mid Oceanic Ridge Basalt (MORB) samples. The older data suggested that δ^{37} Cl values of the depleted mantle can vary between -3 and +0.5% [12–17], although the generally accepted value for the depleted mantle is $-0.2 \pm 0.3\%$ [13]. Cl isotope data from other mantle reservoirs, for example, sampled at Ocean Island Basalts, suggest that Cl isotope values can be as high as +3‰ [16]. Overall, these observations show that δ^{37} Cl in mantle material is highly variable and it is important to understand from what mantle source samples are taken. Based on their data, Pinti et al. [11] suggested a δ^{37} Cl of about +3‰ in the primitive mantle, which is in line with observations by John et al. [16] from Ocean Island Basalts. Although John et al. [16] suggested that these high δ^{37} Cl values resulted from crustal contamination by isotopically heavier halogens from subduction slab metasediments, Pinti et al. [11] suggest as alternative interpretation that the lower mantle feeding the hotspot has (partially) preserved a high- δ^{37} Cl signature of the primitive mantle. This discrepancy in interpretation is thus open for further research. The observations from Pinti et al. [11] may be confirmed by ${}^{3}\text{He}/{}^{4}\text{He}$ and $\delta^{37}\text{Cl}$ data from Northern Portuguese mineral waters [18,19]. Although the highest measured R/Ra (2.7) and δ^{37} Cl (+0.31‰) values presented in studies [18,19] are considerably lower than the highest data observed by Pinti et al. [11], when the trend is extrapolated to an R/Ra of 8 indeed the predicted δ^{37} Cl is about +0.9‰. As the geothermal water samples from Pinti et al. [11] were taken from a continental area in Mexico, they possibly represent better the δ^{37} Cl of the lithospheric mantle, just like in the study by Marques et al. [19]. Both studies are applied to continental areas in either Mexico or Portugal and share comparable positive δ^{37} Cl values. As the Mexican data [11] suggest that δ^{81} Br values are of the same order of magnitude as δ^{37} Cl values, it is suggested that, in other regions, δ^{81} Br should also be comparable. However, as no δ^{81} Br of any mantle derived material has ever been measured, this suggestion could not be confirmed yet.

These relatively high estimates for the mantle [11] are based on the measurement of deep geothermal waters, and not from solid material. In the present study, we present the first ever Br isotope data from Br-rich minerals that crystallised from magmas ultimately derived from the lithospheric mantle. The δ^{81} Br values obtained from these measurements may indicate whether the value suggested earlier [11] can be a reasonable estimation of lithospheric mantle or not.

The only minerals that are known to have been analysed for their Br isotope compositions are evaporite salt minerals. This includes halite, which has very low Br contents [20]. Only in some mantle-derived alkaline rocks a magmatic to hydrothermal Cl-rich mineral (sodalite, Na₈Al₆Si₆O₂₄Cl₂) with sufficiently high Br contents is abundant. A structurally similar mineral (tugtupite, Na₈Be₂Al₂Si₈O₂₄Cl₂) crystallises under hydrothermal conditions only. The Br contents in these minerals vary between 25 and 150 μ g/g [21]. Thus, 0.15 to 1 g of mineral separate is sufficient for Br isotope analysis [5], so that these minerals are a valid target for the determination of Br isotopes in magmatic rocks and hydrothermal systems.

2. Material

Samples used in this study derive from the Ilímaussaq Intrusion (South Greenland), which is one of the most evolved peralkaline intrusions known and contains large quantities of the Cl rich minerals sodalite and eudialyte [22]. For this study, we used previously characterized magmatic and hydrothermal sodalite and hydrothermal tugtupite samples [21]. Magmatic sodalites derive from coarse-grained plutonic rocks that contain abundant euhedral sodalite (up to 70 vol.%) and interstitial alkali feldspar, nepheline, amphibole, and eudialyte. Hydrothermal sodalite and tugtupite samples derive from late-stage cm- to dm-wide veins that crosscut the magmatic rocks and contain variable amounts of sodalite, nepheline, albite, amphibole, and zeolithes [22].

For our study, we selected magmatic sodalite samples with Br concentrations between 100 and 150 μ g/g, and hydrothermal sodalite and tugtupite samples with Br concentrations between 50 and 100 μ g/g. This difference was made, because no more sample material than about 500 mg could be collected from magmatic sodalite. For this reason, magmatic sodalite samples with Br concentrations lower than 100 μ g/g could not be measured. From hydrothermal sodalite and tugtupite, larger sample amounts were available so that 1 g of sample, necessary to measure the δ^{81} Br value, could be collected.

3. Methods

Sodalite and tugtupite are both soluble in diluted nitric acid. For that reason, the technique developed by Eggenkamp and Louvat [5] was chosen to extract Br from the samples. An amount of mineral separate sufficient to collect enough Br for isotope analysis was ground in a mortar and subsequently weighed. The ground mineral was put in a 50-mL two-neck round-bottom flask to which 8 mL Milli-Q water (18.2 M Ω) and 2 mL concentrated nitric acid was added, as well as a few Teflon anti bumping granules to facilitate gentle boiling. The distillation set-up was assembled as described before [5] and consisted of a bridge and a 5-mL plastic vial containing 1 mL of a 0.5 M NH₃ solution as ammonium trap. The sample was gently heated using a Teclu-burner until boiling. The mineral dissolved and bromide present was dissolved in and oxidised to Br₂ by the nitric acid. The Br₂ was distilled to the ammonia trap. In this trap, the Br₂ was reduced to bromide. A small amount of nitrate was also distilled resulting in a bromide containing ammonium nitrate (NH₄NO₃) solution that is ideal to measure δ^{81} Br by ICP-MS [4]. The principle of the Br isotope measurements is described in detail in a prior study [4]. Samples were measured on a Thermo Neptune MC-ICP-MS instrument, which is a double-focusing high-resolution magnetic sector field instrument with an argon inductively coupled plasma and multicollection on nine mobile Faraday cups. Samples were introduced to the mass spectrometer through a small 20-mL cyclonic spray chamber with a 50-µL/min PFA nebuliser. Measurements were performed in low resolution mode. Instrumental mass bias was corrected by sample-standard bracketing. To reduce the memory effect of Br in the introduction system, all Br solutions were prepared with NH₄NO₃ at 0.2 M. The δ^{81} Br measurements were carried out in triplicate for each sample (Std-Smpl-Std-Smpl-Std-Smpl–Std) and reported with an error of two standard deviations. The bracketing standard solutions are prepared to the same Br and Cl concentrations as the analysed samples, to avoid linearity bias and matrix effects. Using this set-up, the internal reproducibility (2SD) over five δ^{81} Br determinations for each sample is usually better than ± 0.15 %.

The Br contents in the original mineral separates were determined by ion-chromatography on the NH_4NO_3 solutions and calculated back to the amount of mineral separate used for Br extraction.

4. Results

Br concentrations and δ^{81} Br values change systematically between the three sample types (Table 1, Figure 1). δ^{81} Br values are lowest in magmatic sodalite samples, slightly higher in hydrothermal sodalite samples, and significantly higher in the (hydrothermal) tugtupite samples. Br concentrations are highest in the magmatic sodalite samples and are lower in hydrothermal sodalite samples, and even lower in tugtupite samples. Hydrothermal sodalite samples and even lower in tugtupite samples. Hydrothermal sodalite samples and more in line with that for tugtupite. Br concentrations measured after HNO₃ extraction were like those measured after WO₃ combustion (Table 1), except for magmatic sodalite, where they seem to be higher by a factor of about 1.2. These differences are probably an extraction artefact. As the analytical data obtained by the two extraction methods are comparable, we use the data published in our recent study [21] in the discussions throughout, to maintain consistency between the two studies.

Table 1. Results of the Br determinations and δ^{81} Br measurements of the sodalite and tugtupite samples measured in this study, based on ion-chromatography after HNO₃ extraction. Data in the row after the names of the sample groups are averages \pm the standard deviations of the Br⁻ and δ^{81} Br values of all samples within each sample group.

Sample	Br ⁻ (μg/g) [21]	Br [–] (µg/g), This Study	δ^{81} Br (‰ vs. SMOB)
Magmatic sodalite	Avg = 138 ± 10	Avg = 172 ± 21	Avg = 0.23 ± 0.07
2016-73	122	159	0.29 ± 0.11
2016-78	146	178	0.15 ± 0.11
2016-85	135	148	0.24 ± 0.04
2016-87	148	173	0.16 ± 0.06
2016-96	140	204	0.31 ± 0.04
Hydrothermal sodalite	Avg = 53 ± 10	$Avg = 49 \pm 8$	$Avg = 0.36 \pm 0.08$
ILM123	55.3	53.4	0.32 ± 0.12
ILM138	45.0	57.2	0.45 ± 0.06
ILM158	44.1	36.2	0.26 ± 0.15
ILM162	50.8	48.8	0.33 ± 0.08
GM1246	68.3	49.4	0.43 ± 0.05
Tugtupite (hydrothermal)	$Avg = 26 \pm 2$	Avg = 34 ± 8	$Avg = 0.71 \pm 0.17$
KK1	27.7	39.7	0.59 ± 0.09
KV1	24.8	28.6	0.83 ± 0.03
ILM127 (hydrothermal sod.)		$Avg = 24 \pm 2$	Avg = 0.82 ± 0.12
(1)		25.8	0.69 ± 0.47
(2)	47.7 ± 9.2	22.2	0.85 ± 0.27
(3)		24.1	0.92 ± 0.10



Figure 1. Relationship between the Br content and the δ^{81} Br of the sodalite and tugtupite samples measured in this study. Minerals crystallised at later stages have lower Br concentrations and higher δ^{81} Br values.

5. Discussion

No Br isotope values of silicate minerals had been published before. Only from evaporite minerals Br isotope measurements are available, and these reflect the Br isotope evolution of individual sedimentary basins or geological periods [20]. Based on these data, it was concluded that the Br isotope compositions of the oceans was, at most, slightly higher (probably 0 to +0.25‰ vs. SMOB) than today's value and did not change significantly during most of the Earth's history. This suggests that long term Br isotope fractionation between the surface reservoirs (mostly ocean water) and upper mantle reservoirs through the process of subduction is negligible.

Br isotope values and Br concentrations are summarised in Figure 1. δ^{81} Br values of the magmatic sodalites in our sample set are between 0.15 and 0.31% with an average value of 0.23 \pm 0.07%. Magmatic sodalite in the Ilímaussaq intrusion crystallised from the final differentiation stage of the magma [21].

In general, Cl and Br concentrate in evolving magmatic systems as both elements are incompatible in most minerals during magmatic differentiation. Depending on the redox state of the magma, halogens either concentrate in aqueous fluids (oxidising conditions) as they are strongly soluble in water, or they concentrate in the melt (reducing conditions), when fluids mostly consist of methane, in which halogens are largely insoluble [23]. Under the latter conditions (that apply for Ilímaussaq [22]), Cl-rich silicate minerals, such as sodalite group minerals (SGM; with up to 7 wt.% Cl) and eudialyte group minerals (EGM, with up to 1.5 wt.% Cl), may form. These two mineral groups host most Cl and Br that was present in the melt, as the two elements show very similar behaviour in magmatic processes [24]. Importantly, SGMs take up Br preferentially compared to EGMs [21]. It is assumed that Br concentrates in the final melt from which SGMs (in principle sodalite proper) crystallise, as it is generally assumed that little Br is removed from the melt before sodalite crystallises. Still, changes in Br contents and isotope composition will reflect processes such as melt extraction, interaction with asthenosphere melts, interaction with subducted materials, and degassing [17,25–27]. The average δ^{81} Br in the magmatic sodalite samples is +0.23^{\overline}. While this δ^{81} Br value is representative for the parental melt, it is not the same, as, during crystallisation, isotope fractionation takes place.

In the case of Cl, sodalite–melt isotope fractionation has been estimated in experimental and theoretical studies [12,28–30]. Equilibrium isotope fractionation of Cl between sodalite and various other phases, such as liquid NaCl, gaseous HCl, hydrated Cl ion, and other Cl-bearing minerals invariably points to lower δ^{37} Cl values in sodalite as compared to the other phases. Although sodalite–chloride fractionation factors determined in these studies varied significantly depending on phase and temperature they suggest that δ^{37} Cl of sodalite is in the order of 0.3‰ lower than the phase it is in equilibrium with, and we suggest that this is also a reasonable approximation of the equilibrium fractionation between sodalite and the melt from which it is in equilibrium.

Recently, a study was published [10] that described theoretical calculations of Br isotope fractionation factors mostly for evaporite minerals. The results obtained from the calculations suggest only small fractionation factors between salt and brine and results suggest lower fractionation factors than obtained in earlier experimental studies [31]. Calculated data on Br doped Cl minerals suggest that Br isotope fractionation factors in these minerals are larger than those for pure Br minerals. This agrees with Br isotope measurements in natural evaporite systems [32,33].

Br isotope fractionation in naturally occurring evaporite minerals in equilibrium with salt-saturated aqueous solutions is similar to or slightly larger than Cl isotope fractionation [32,33]. Salt–water fractionation and silicate–melt fractionation are basically similar processes as in both processes two phases are present, one in which Cl is present as freely moving Cl ion (with or without a hydration shell) and one in which Cl is bound in a crystal lattice. Assuming that the isotope fractionation effect between saturated solution and salt can be applied (or be approximated) to sodalite in equilibrium with melt too, Br isotope fractionation between crystal and melt can be estimated as -0.3%, which indicates that δ^{81} Br of the melt is about +0.5 to +0.6‰, which would, if the melt is representative for the lithospheric mantle, represent a possible lithospheric mantle value. This value agrees well with the value of +0.7‰ as suggested by Pinti et al. [11].

We are cautious in suggesting that a value obtained this way is representative for the lithospheric mantle. Although the melt from which sodalite crystallised is sourced from the lithospheric mantle, the composition of the residual melt may have been changed considerable before the first sodalite crystallises from this melt. Furthermore, considering the related element Cl, it is shown [17] that not only do the δ^{37} Cl of the various mantle reservoirs show large variations, but also that variations within individual reservoirs can be significant. As a result, a single datapoint cannot be used to define the (average) value of the (lithospheric) mantle. This is also applicable to Br isotopes. As our value is in line with that from Pinti et al. [11], it is reasonable to conclude that δ^{81} Br values between +0.5 and +0.7 are within the lithospheric mantle range. It is clear however, that more Br isotope research on mantle material is necessary to start to understand the δ^{81} Br distribution in the mantle.

While magmatic sodalite crystallises at temperatures between 650 and 825 °C [34], hydrothermal sodalite crystallises at temperatures down to about 400 °C and hydrothermal tugtupite at even lower temperatures, but only when Be concentrations are sufficiently high [35].

During cooling, the Ilímaussaq magma became more reducing until a temperature of about 700 °C, after which the oxygen fugacity rose again [36]. Below a temperature of about 550 °C, the oxidation stage was high enough to facilitate the exsolution of Cl-rich and water-dominated magmatic fluid [37]. Although the magma had solidified at this point, reactions between dissolved Cl and nepheline produced hydrothermal sodalite to temperatures down to about 400 °C. If Be concentrations were high enough, tugtupite also formed at temperatures below about 500 °C down to temperatures even lower than those for sodalite [36].

 δ^{81} Br of hydrothermal sodalite is higher than δ^{81} Br of magmatic sodalite (+0.36 vs. +0.23‰, Figure 1), while the Br content is significantly less. In tugtupite, the average δ^{81} Br is even higher at +0.71‰ and the Br concentration is lower than in hydrothermal sodalite. This suggests that more Br is preferentially incorporated in sodalite and thus removed from the fluid phase during crystallisation of sodalite. As the δ^{81} Br of the mineral phases increase during evolution from magmatic to hydrothermal sodalite and to tugtupite, this suggests that the light isotope (⁷⁹Br) is preferentially removed from the fluid δ^{81} Br increases, so that, assuming a fractionation factor that only slowly increases towards lower

temperatures, later crystallising sodalite becomes isotopically heavier. This confirms the suggestion made above that Br isotope fractionation is negative during crystallisation of sodalite and tugtupite from its coexisting fluid, something that is schematically shown in Figure 2. As isotope fractionation factors increase towards lower temperatures, the Br isotope fractionation factor also increases during this process, and we suggest that its value might increase to -0.4 to -0.5% in the latest stage when tugtupite crystallises. It is very important, however, that future experimental and theoretical studies will focus on the determination of the actual fractionation factors at different temperatures for both magmatic and hydrothermal processes.



Figure 2. Schematic view of Br isotope evolution from magmatic sodalite, via hydrothermal sodalite to tugtupite (and ILM127). The lithospheric mantle from which the Ilímaussaq melt was sourced has a value of +0.5 to 0.6‰, from which magmatic sodalite crystallised with a fractionation factor of about -0.3%, giving it the average measured δ^{81} Br of +0.23‰. Because light ⁷⁹Br is preferentially removed from the fluid phases, the δ^{81} Br of the residue increases, which leads to higher δ^{81} Br values in sodalite that later crystallised. This evolution continues to the last stages resulting in tugtupite (and perhaps sodalite from fluids that do not contain enough Br to crystallise tugtupite from) with the highest δ^{81} Br values.

Sample ILM127 is a hydrothermal sodalite and is used as internal standard in our laboratory. For that reason, this sample has been analysed three times to test the quality and integrity of the Br isotope measurements. The three measurements confirm the high δ^{81} Br of this sample. The δ^{81} Br of this sample compares well to the δ^{81} Br of the tugtupite samples. This suggests that ILM127 is a highly evolved sodalite sample that crystallised from a fluid that, due to a low Be concentration, has not been crystallised as tugtupite. However, as it crystallised from the last and coolest hydrothermal stage, it has the same Br isotope characteristics as tugtupite. This scenario might exist at temperatures of around 400 °C [36].

6. Conclusions

We measured δ^{81} Br for the first time from magmatic and hydrothermal minerals (sodalite and tugtupite). The data obtained allow us for the first time to suggest values for the Br isotope fractionation between melt and sodalite. This fractionation can be constrained based on the evolution from magmatic sodalite to hydrothermal sodalite and tugtupite. During this evolution, δ^{81} Br of the mineral phases increases, suggesting a negative fractionation factor. δ^{81} Br values obtained in this study and comparisons with recent studies on Cl and Br isotope fractionation suggest that fractionation factors of about -0.3% for fractionation between melt and magmatic sodalite, and possibly -0.4 to -0.5% for fractionation between fluid and hydrothermal minerals at lower temperatures can be constrained. Based on an average δ^{81} Br of +0.23% for magmatic sodalite, the δ^{81} Br of the melt is between +0.5 and +0.6%. This value is similar to a value of +0.7%, as

obtained by Pinti et al. [10]. This suggests that δ^{81} Br values between +0.5 and +0.7 are within the lithospheric mantle range. Just like is the case for Cl isotope variations, it must be realised that the actual Br isotope range of mantle materials can be considerable and significant further research is necessary to define the range of δ^{81} Br variations, not only for the lithospheric mantle, but also the various other mantle reservoirs.

The evolution from magmatic to hydrothermal sodalite and to tugtupite at ever lower temperatures results in continuously decreasing Br concentrations in the subsequent minerals and continuously increasing δ^{81} Br values. This indicates that Br is depleted in the residual fluid and that (lighter) ⁷⁹Br is incorporated preferentially in the minerals. This results in increasing δ^{81} Br values in subsequently crystallising minerals and implies that Br isotope fractionation is negative in both magmatic and hydrothermal processes.

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Data Availability Statement: All data collected for and used in this study is contained within the article in Table 1 and ref. [21].

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