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Comment on egusphere-2022-676

Fiz F. Perez (Referee)

Referee comment on "Oceanic Alkalinity and Titration Alkalinity and the small difference between them due to minor effects of sulfate, fluoride and phosphate in the acid titration of oceanic seawater" by Hein J. W. de Baar et al., EGU sphere,
<https://doi.org/10.5194/egusphere-2022-676-RC1>, 2022

Title: **On the true and the perceived minor interactions of dissolved phosphate and dissolved sulphate and some other constituents with the Alkalinity of oceanic seawater**

Authors: **Hein J.W. de Baar, Mario Hoppema and Elizabeth M. Jones**

Revision by Fiz Fernandez Perez (Instituto de Investigaciones Marinas, IIM-CSIC)

The attached pdf contains links and allows reading in another format.

General Comments

Stating that there is some confusion in the literature, the authors propose to recover in an operational way the classical definition of total alkalinity in seawater, based on the charge balance defined as the difference between the sum of fully dissociated strong cations and fully dissociated strong anions. They call it oceanic alkalinity (OA) and propose that it be determined by acid titration. In the marine environment, biological mineralization of organic matter generates very small amounts of sulfate and phosphate. While the latter would have no effect on OA, the former would have a very small effect on the order of OA accuracy. However, both are considered in the classical operational definition of total alkalinity (TA) of Dickson et al. (1981), based on acid titration of seawater using the balance of hydrogen ion acceptor and donor species. In order to achieve full consensus among ocean scientists the authors suggest to remove the theoretical difference between the two definitions, OA and TA, motivates the authors to question the role of sulfate, phosphate and nitrite species in the TA definition, and of the relevant sulfate formation

during organic matter mineralization processes.

The classic definition of TA (Dickson et al. 1981) has been in operational use for four decades by the scientific community with hundreds of thousands of measurements reported in international databases and certified reference materials (CRMs) used for quality control. TA is well established in the scientific community, in terms of its theoretical definition, and there is a strong family of computer software based on CO2SYS (Lewis and Wallace 1998). There are some practical problems that the scientific community has been evaluating, such as the effect of organic acids in the determination of TA, or a more precise knowledge of the total borate concentration, or those related to the establishment of a pH scale based on the concentration of 'free' hydrogenions. They all impact the internal consistency of the seawater carbonate system at levels very close to the accuracy of TA and DIC measurements. However, these are not the elements discussed by the authors in the manuscript. They propose to eliminate in the definition of TA certain chemical species (whether or not in ionic form) so that the definition of TA and OA are equivalent. Previously Middelburg et al. (2020) have discussed about the concept of OA (Ocean Alkalinity) based on alkalinity charge balance (CBA) following a previous article by Soetaert et al. (2007) where it is evaluated how natural processes (biological or not) affect differently CBA and TA. In fact, the differences in TA and CBA shown by Soetaert et al. (2007) are identical to those shown by Wolf-Gladrow et al. (2007) systematically questioned in the present manuscript. Both papers, the one by Soetaert et al. (2007) as well as the one published in 2020 in *Reviews of Geophysics* by Middelburg et al. are, surprisingly, neither cited nor discussed at any point in the entire manuscript.

Dealing with many aspects of very little effect on alkalinity, the article must address a multitude of processes, which makes it lengthy and, in some ways, wordy. The manuscript analyzes in great detail different articles concerning the biological processes that generate small amounts of sulfate from organic matter, to finally propose that this contribution is so small as to be negligible. It is true that many articles do not evaluate or ignore the sulfate contribution considering mainly nitrate and phosphate, but there are several classic articles (Chen 1978; Kanamori and Ikegami 1982; Fraga and Alvarez-Salgado where it is evaluated from the biochemical composition of organic matter, with S:P ranges varying from 1 to 2.8. This suggests that the sulfate generation suggested by Wolf-Gladrow et al. (2007) and reflected in TA dynamics in other papers (Carter et al. 2014 and Lauvset et al. 2020) has to be taken into account although its impact on sulfate concentration is practically negligible and therefore on OA.

In fact, I believe that the effort to unify the definition of ocean alkalinity is probably futile because while the titration-based definition is clearly proven, and in general use and consistent with other measures of the marine carbonate system, the AO proposal based on the definition of strong anions has certain weaknesses. There are ionic species such as chloride, nitrate or sulfate that clearly fall into that category, but others such as bisulfate, fluoride, nitrite, or H_2PO_4^- since they may consume a small percentage of the acid load that is realized during titration of seawater that reaches $\text{pH}=3$. The definition itself has a significant asymmetry since also certain majority cations considered 'strong' have significant interactions with $[\text{OH}^-]$ but this has no impact on the differences between OA and TA.

Consequently, the current manuscript, despite the debate it generates, proposes a definition of alkalinity that is not operative and is not clearly supported despite the important discussion on a significant list of articles that suffers from the lack of the most relevant ones.

Specific Comments

Line 15: Change "interactions... with alkalinity" to "contributions... to alkalinity". Alkalinity is not a chemical species that interacts with any other.

Line 22: "Oceanic Alkalinity can be determined by acid titration of a seawater sample, this leading to an ensuing value of Titration Alkalinity." While Middelburg et al (2020) show that both definitions do not lead to identical alkalinity values, de Baar et al. state the opposite.

Line 27: "To the best of our knowledge, this perceived role is mistaken". No reason or argument is shown when many other authors have evaluated experimentally or theoretically the contribution of phosphate. (e. g, Kim et al. 2006, and Kanamori and Ikegami 1982, Fraga and Alvarez-Salgado 2005)

Line 30-33 "Moreover, the role of sulphate is not verifiable, because the small amount of biological assimilation of sulphate cannot be discerned from measurement of the very large background concentration value of dissolved sulphate". The need to include the sulfate ion, and specifically the bisulfate ion in the alkalinity titration equation comes from the very small formation of HSO_4^- contributing importantly (30%) to the concentration of total hydrogen ions affecting the alkalinity determination which is performed between pH=3 to pH=4.

Line 34 "but insignificant versus the accuracy of the measurements of Titration Alkalinity" $\text{pK}(\text{Nitrite})=3.2$ below 4.5. So its contribution to TA is practically the same as that of nitrate, although it is not a strong acid (like nitric), it is 500 ($10^{2.7}$) times stronger than $\text{CO}_{2(\text{aq})}$ (K_1). On the other hand, if the theoretical incorporation of nitrite is not incorrect, there is no room for discussion of its inclusion in the alkalinity equation, whether it is significant or not.

Line 36 "the negative sign of $[\text{H}_3\text{PO}_4]$ is mistaken.." The pK_1 (=1.8) of H_3PO_4 is very similar to the pK of HSO_4^- (=1.0), so theoretically it should be included regardless of the impact of the mineralization of phosphorus compounds present in the organic matter and

which are susceptible to be mineralized to H_3PO_4 .

Line 60 "quantifying the formation/dissolution of CaCO_3 one cannot detect directly the related changes in the concentration of dissolved calcium (Ca^{2+}), because these changes are not discernible versus the very large background...". It seems that nearly 40 years ago **Kanamori and Ikegami (1982)**, none cited in the manuscript) were able to do that.

Line 92-93 'In order to unravel the various components of the DIC pool, there are four key variables that can be measured directly in a collected sample of seawater'. I guess the authors are unaware that it has also been possible to measure carbonate ion for 14 years (Byrne and Yao, 2008; Gualart et al. 2022).

Line 97-102: This paragraph proposes without clear relation to the previous paragraphs that the exact value of alkalinity is unclear because of the biological role of sulfate and phosphate citing only Wolf-Gladrow et al. 2007. In a review article in the journal 'reviews of Geophysics' Middelburg et al. 2020 (not cited in the manuscript) argued very similarly to Wolf-Gladrow et al. 2007. The Wolf-Gladrow et al. 2007 ratios or similar has been used in Lawset et al. (2020) and Carter et al. (2014) (none cited in the manuscript)

Line 116. Equation 1. This equation (Redfield et al. 1963) was revolutionary at the time, but not very accurate in the way it expresses the "average" organic matter (OM) mineralized in the aphotic layer of the ocean. It simulates that the OM is composed of phosphoric acid, ammonium and carbohydrates. Although this is not an easy task as it is necessary to know the average biochemical composition of marine plankton, several authors have already expressed this 'stoichiometry' in a form closer to reality (e.g. Fernández-Castro et al. 2019, Alvarez-Salgado et al. 2014; Hupe and Karstensen 2000; Anderson et al. 1995, Rios et al. 1998, and others). It is advisable to at least use the equation of Anderson et al. (1995) more in line with the biochemistry observed in OM or at least use a condensed form of the Redfield et al. (1963) expression.

Line 149. Equation 7 is not a chemical equilibrium expression, this should be a mathematical expression. Please replace both opposite arrows by equal one. I believe that the detail shown in this part of the manuscript is somewhat avoidable and that equations 2 to 7 could easily be omitted.

Line 177 'proton concentration [H^+]. Change to 'Hydrogen ion concentration'. Interactions between chemical species occur through the exchange of electrons in the valence layer. The proton refers to the elementary particle present in the nucleus of the atom. Therefore, the use of the term proton to refer to H^+ should be avoided. It certainly exists in the classical definition of acid and base by Brønsted (1923) and Lowry, 1923, as the transfer or donation or reception of protons. However, it is still a concept overcome by Lewis (1923) who defines an acid as a chemical species containing an empty orbital capable of accepting an electron pair from a base. It is practically impossible to describe the presence of a free proton as a subatomic particle in a condensed phase such as pure water or

seawater. As far as we know, water molecules dissociate by transferring a hydrogen atom with an empty orbital to a neighboring molecule that gives up a pair of electrons from the valence shell of the oxygen atom, generating OH and H₃O⁺. Let us say that the hydrogen bridge bonds between the water molecules are activated upon a transfer of the hydrogen atom, resulting in the sharing of a pair of electrons given up by the oxygen of the neighboring molecule that yields its electron to the oxygen from which it dissociates. This type of electronic interactions also explains the high ionic mobility of the hydrogen ion in water (Grotthuss mechanism). It is recommended to follow the IUPAC and use the oxonium ion (H₃O⁺) which was previously called hydronium ion.

Line 187 'free protons..'. Change by oxonium or hydrogen ions.

Line 255. I wonder if the interactions of Ca²⁺ and Mg²⁺ with OH⁻ to form OHCa⁺ and OHMg⁺ are not equally relevant as that of HSO₄⁻, and if this does not somewhat invalidate the definition of Alkalinity based on charge balance.

Line 326-328 'Conversely, one realizes that these latter four systems are not, or virtually not, making a significant contribution to Titration Alkalinity in well oxygenated seawater. However, they are necessary in their analytical determination considering that the pH equivalence is normally determined in the pH range of 3-4 or 3-4.5, and because both bisulfate and HF contribute to capture a 30 and 2% of the acid load, or in other word they contribute to reduce the 'free' hydrogen ion concentration. Or in other words, a relevant part of the HCl contribution is mobilized in the increase of their concentrations.

Line 347-348 '~10^{-4.5} μmol.kg⁻¹' and next lines. The symbol 'micro' have to be deleted. Both hydrogen ion and bicarbonate concentration would be around 31.5 μmol.kg⁻¹, being de CO₂(aq) nearly 1968 μmol.kg⁻¹.

Line 359 'which the square root is ~1.4 x 10^{-4.43}'. That is a pH=4.28.

Line 361-22 'However, strictly speaking, Dickson (1981) did somewhat simplify by stating pH = 4.5 as the endpoint,...'. This is not true. Dickson sets pK values to distinguish between chemical species that do or do not contribute to alkalinity, but does not set any endpoint. Moreover, the final pH will depend on the very chemical and physical characteristics under which the titration is performed, which are usually below pH=4.5.

Line 365-366 '(The simplification by Dickson (1981) and earlier articles, may, or may not, relate to the fact that initially the end-point was determined by linearization rather than curve fitting of the titration curve.). This is rather speculative and unsubstantiated.

Line 458 The carbonate ion concentration can also be measured. This means that there are five and not four CO₂ system variables that can be measured.

Line 505- 516 Chen et al. 1982 is very crystal clear in the page 2 of the article 'To conclude, neglecting the small amount of calcium phosphate dissolution, the release of one mole of H₃PO₄ due to organic matter decomposition decreases TA by one equivalent according to the current method of determining TA. Arthur Chen himself has confirmed this via email. In any case, there is more research and articles not evaluated in the manuscript that show that the contribution of phosphate and even sulfate generated by the oxidation of organic sulfur compounds should be included as alkalinity sinks (Kanamori and Ikegami 1982; Kim et al. 2006, Alvarez-Salgado and Fraga, 2005). In the specific case of Kanamori and Ikegami it is shown experimentally with correlations with Ca⁺² observations.

Line 517-524. In relation to Brewer articles: Brewer et al. 1975 "This postulates an effective flux of nitric and phosphoric acids into the deep water. Other redox changes, such as in the oxidation of reduced sulfur, may also contribute protons, but these are more difficult to evaluate" and "The true amount, here referred to as the "potential alkalinity", is unknown. We can attempt to calculate it through the application of additional terms to compensate for proton transfer. The simplest form of this equation would be as in (6): $\Delta PA = \Delta TA + 1 \Delta NO_3^- + 1 \Delta PO_4^{3-}$, where ΔPA and ΔTA are the potential alkalinity and alkalinity differences, in/leq/kg, between two water masses, and ΔNO_3^- and ΔPO_4^{3-} are the nitrate and phosphate differences, in micromoles/kg, between the same two water masses." Why the authors do not cite and comment these piece of literature about that?

Line 533-534 "Most relevant here is that the uptake or release of phosphate is not mentioned at all, therefore does not affect Oceanic Alkalinity." This is not fair. The fact that many authors have not considered the impact of the mineralization of phosphorus compounds on alkalinity because of its small magnitude does not mean that these authors consider that it does not affect at all.

Line 533-556. Many authors have considered the variation of the sum of alkalinity + nitrate referred to a fixed or reference salinity as a way to evaluate the changes due to CaCO₃ dissolution without including phosphate. I have done this myself many times, but this does not mean that these same authors consider that there is no phosphate contribution but that it is insignificant. Many times, it has been based on a simplification of the calculations especially if we talk about several decades ago where the numerical calculation was not as affordable as now, or even because there was no quality phosphate data available to substantially improve the results.

Line 620-621 'Thus, for normal seawater in the world oceans, the H₃PO₄ term in the Titration Alkalinity Eq. (24) is merely theoretical and practically at best leading to

confusion for some readers.' It is correct that the concentration of H_3PO_4 is very small in the final part of the titration curve (pH between 3 and 4.5), representing only 0.006% of the hydrogen ion concentration, while for HSO_4 and HF it is 30% and 2% respectively. However, this does not mean that this is an error, it simply means considering that a small part of the acid added during titration will be consumed to produce H_3PO_4 even in very very small quantities.

Line 622 'Another cause of confusion is the negative sign for the $[\text{H}_3\text{PO}_4]$ term in Eq. (24).' The negative value is intrinsic, for the reasons given above, to the definition of total or titrated alkalinity being fully consistent with the CO2SYS software for a global community that has been used to check the quality of observations made globally for more than 4 decades.

Line 636. "In other words, the negative sign of $[\text{H}_3\text{PO}_4]$ in the Eq. (24) is mistaken and yet another reason". Again, just because this term is very small and negligible does not mean that its sign is an error. This argument is flawed.

Line 690-692 "The exact determination of all these changes can be done by a computer chemical speciation program, for example MINEQL, or the CO2SYS algorithms that are tailored for the key variables of the CO_2 system in seawater." Certainly, these algorithms are fully compatible with Dickson's (1981) definition of alkalinity and less so with the one based on the charge budget alkalinity (CBA) supported by the authors.

Line 704 "This sub-chapter is one of two pivotal sections" After of reading the half of the manuscript, the hypothesis of the manuscript is present. This is based on a somewhat forced reading of some classic articles and ignoring others such as Soetaert et al. 2007 and Middleburg et al. 2020 where the objective of the manuscript is treated with much greater detail and precision.

Line 725-727 However, Wolf-Gladrow et al. (2007) have presumably overlooked the later paper by Chen et al. (1982) which rejects, and thus effectively retracts, the earlier suggestion that phosphate uptake/release does affect ocean alkalinity by Chen et al. (1978)." Chen et al. do not reject the role of phosphate (personal communication), so Wolf-Gladrow et al. are not wrong. See also Soetaert et al. 2007.

Line 775 'Therefore, nitrite does not significantly affect the value of Titration Alkalinity'. Since nitrite ion can associate with hydrogen ions to a concentration-dependent extent at pH below 4.5 (nitrite can consume part of the hydrogen ions supplied during titration), it must be incorporated into the titrated alkalinity as indicated by Wolf-Gladrow et al. 2007. See also Soetaert et al. 2007.

Line 842 'where the hydrogen ion concentration is expressed on the "free" scale'. Here it is

very well expressed, not "proton concentration".

Line 860-863 "This is well above the accuracy of Titration Alkalinity. In other words, a small ($\sim 0.3\%$) portion of the sulphate has absorbed some protons and this is accounted for by the term $[\text{HSO}_4^-]$ in the overall Eq. (24) of Titration Alkalinity. In summary, all chemical oceanographers fully agree that sulphate is a strong anion in natural seawater ($\text{pH} \sim 8$) but has absorbed some protons at $\text{pH} = 4.5$." It is correct that sulfate absorbs 30% of the hydrogenions added during the alkalinity titration. I do not fully agree that sulfate is a strong anion. The authors seem to relativize the characterization of strong anion as a function of pH. It is strong at $\text{pH} \sim 8$ but not at $\text{pH} = 4.5$. Does this not call into question the definition of alkalinity as a function of the sum of strong cations minus strong anions since it is pH dependent? What about cations: many of them present high percentages in terms of OH^- of CaOH^+ or MgOH^+ associations and that at $\text{pH} \sim 8$ can mean a few tenths of micromol/kg which are much larger magnitudes than those given in the manuscript in relation to phosphate.

Line 872-3 "These stoichiometric relationships of C/N/P/Si are based on the oceanic distributions of dissolved constituents in seawater." Stoichiometry refers to the molar ratio of a chemical reaction or a 'set of them' meaning a process of biochemical transformations involved in the formation or mineralization of the MO. Oceanic distributions show relationships or ratios (no stoichiometric relationships) between nutrient concentrations and these do not necessarily reflect each other. In fact, for N/P there seems to be some agreement with the eq1 but not for C/Si or C/P.

880-882 "In contrast, the dissolved constituents DIC, nitrate, phosphate (and silicate), due to ocean mixing processes that serve as an averaging tool, have already arrived at a mutual stoichiometry (Equation 1) that is very accurate with very low standard deviations." This suggests to me that the authors do not have a complete understanding of how eq.1 is obtained, and that they are unaware of the state of the art in this matter. There are two ways: by analyzing anomalies in the mixing of water masses (ref.- Takahashi et al. 1985, Anderson and Sarmiento 1994; Alvarez-Salgado et al. 2014, Hupe and Kartensen 2000; Fernandez-Castro et al. 2019, and many others), or by studying the mean composition of organic matter (Laws 1991, Anderson 1995; Fraga et al. 1998; Rios et al. 1998,...). Moreover, the standard deviations are not 'low' but rather in the order of 10 to 20% depending on the methodology and the geographical area.

886-893: This paragraph is not relevant for the objective of the manuscript.

894-901: In this paragraph, the authors seem to argue that the stoichiometric ratio in which plankton utilize the various elements should be reflected in the ratio of concentrations present in the water. They seem to extrapolate what happens with the N:P ratio in a rough way and with other micro or trace elements in a clearly incorrect way since many of the elements (or major elements) present in seawater are not related to biological activity but to other geochemical processes of very long-time scale.

902-915: It is very likely that the stoichiometric ratio S:P=2.4 of Wolf-Gladrow et al. 2007 is in the high range. Not only from Finkel et al. 2006, but also if one considers Kanamori and Ikegami's Alk:NO₃ ratio of 1.26 which would imply an S:P=1.6, right in the upper range of Finkel et al. 2006. As early as 1978 Chen 1978 also uses the ratio S:P=1.6. However, estimation of this ratio is somewhat complex due to the difficulty of assessing the variability of sulfur compounds, such as DMS, in marine plankton. Fraga and Alvarez-Salgado (2005) have evaluated S:P ratios in function of the DMSP produced by the phytoplankton, given values of 2.3, 3.3 and 5.7 micromol of H⁺ per mol of mineralized phosphorous which is comparable to the value of 1.4 micromol of H⁺ obtained for phytoplankton that does not produce DMSP. Furthermore, arguing that "In other words, hypothetical sulfate concentration changes of biological origin are not verifiable because they are undetectable" is meaningless given that high sulfate concentrations in water come from non-biological sources.

Line 920-922 "Last but not least, throughout the existing literature the Oceanic Alkalinity has always been defined without taking into account this more recently suggested (Wolf-Gladrow et al., 2007) effect of biological uptake/release of sulphate". At least two published articles (Carter et al. 2014; Lauvset et al. 2020) have used ratios ALK:N base in Kanamori and Ikegami and Wolf-Gladrow et al., (2007).

Line and 989 and 1027 $+[\text{Sr}^{2+}]$ should be $+2*[\text{Sr}^{2+}]$ eq. 20 a 44

Line 1016 $'[3\text{PO}_4^{3-}]'$ should be $3*[\text{PO}_4^{3-}]$

Line 989-1041. The development of Wolf-Gladrow et al., 2007 is correct. It starts from the zero-charge equilibrium as the electroneutrality condition for seawater (equation 31 in Wolf-Gladrow et al., 2007 and equation 42 in the present work). He then tries to include Dickson's (1981) definition of total alkalinity to obtain his equation 32. In that expression he compares the differences between the charge budget of the strong ions with the total alkalinity. Somewhat similar to the present manuscript is the equation of Soetaert et al. 2007 in their Table 3. Also, Middleburg et al. 2020, equation 7 compares TA with CBA (or also called excess negative charge-ENC of Soetaert et al.). Besides ignoring or not knowing the two articles mentioned above, perhaps the mistake of this manuscript is to try to equate their equation 20, their definition of Oceanic Alkalinity with Total Alkalinity as they are different magnitudes.

1102-1105 'In contrast, the article by Wolf-Gladrow et al. (2007) largely focused on the biomass domain with an assumed requirement of overall neutral electric charge balance of the plankton biomass. The latter various neutral charge balance reasonings for marine plankton are not necessarily valid, and also not necessarily all verifiable.' The paper by Wolf-Gladrow et al. (2007) did not focus on the overall neutral electric charge balance requirement of the biomass but on that of the water mass.

1111-1112 "With respect to alkalinity A_q these factors +0.21 and -0.21 are wrong." This

is not so clear, it may be perhaps somewhat high.

1177-1181. "Unfortunately, these recent findings of excess Alkalinity in the CRMs appear to be a caveat. Matters are complicated also because different batches of CRMs tend to show different values of such excess Alkalinity. Finally, historically there have been previous suggestions of interferences. Nowadays these are deemed to be merely of historical interest. Nevertheless, one example of such historical suggestion is described in Supplementary Material C." This is an interesting reflection on the work of Sharp and Byrne (2021), although I think it is somewhat exaggerated. That study has not evaluated the impact of the addition of HgCl_2 to CRMs (~ 33 micromolar) so some differences might be expected. It also shows that it is possible that the existence of possible amounts of organic matter that can act as weak bases (hydrogen ion acceptors) is likely to be very small in natural waters, lower than those predicted in Fong and Dickson (2019). The usefulness of CRMs is and has been of great relevance for obtaining high quality data from marine carbonate system, and the possible uncertainties of CRMs, if any, should be endorsed in future work.

1190-1191 'Currently, the perceived role of biological uptake or release of dissolved phosphate in the value of Oceanic Alkalinity is often mistaken, which may be due to two articles with great influence in the biogeochemistry community.' It is true that the impact of phosphate formation by biological mineralization of OM does not affect OA as defined by the authors, but it does affect total alkalinity or titrated alkalinity as commonly measured in oceanographic studies, and which are subsequently used along with other marine carbonate system variables to study their variability.

1196-98 'The perceived role of biological uptake/release of dissolved sulphate from seawater is not verifiable because it cannot be discerned from measurement of the relatively very large background dissolved concentration value of sulphate.' This fact has been observed, and evaluated by several authors since 1978 (Chen 1978; Kanamori, S. and Ikegami, H.1982, Kim et al. 2006, Alvarez-Salgado and Fraga 2006) and used in several articles such as Carter et al. 2014, Lauvset et al. 2019.

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Hydronium ion IUPAC oxonium <https://es.wikipedia.org/wiki/Oxidanio>

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