Supporting Information

A simple yet effective chromogenic reagent for the rapid estimation of bromate and hypochlorite in drinking waters

Zhang Jia and Yang Xiurong*

*Correspondence e-mail: xryang@ciac.jl.cn

1. Experimental section

1.1. Reagents and apparatus

3,3',5,5'-tetramethylbenzidine (TMB), sodium hypochlorite, and sodium nitrite were purchased from Sigma-Aldrich chemical company, Inc. (USA). Potassium bromate, hydrochloric acid (12 M), and other inorganic chemicals were obtained from Beijing Chemical Reagent Company (China). They were all used without additional purification. Ultrapure water (18.2 MΩcm) was used throughout the experiment. The room temperature at which the experiment was conducted was 24 ± 1 ^{o}C. The stock solution of TMB (0.6 mM) was prepared in diluted HCl (0.02 M). The hypochlorite stock solution was prepared by spiking 10 μL concentrated NaOCl solution to 1 mL NaOH solution (pH = 12). The working hypochlorite solution was freshly prepared by water-dilution of the stock solution whose concentration was determined by the UV absorbance at 292 nm using the molar absorptivity equal to 350 $M^{-1}cm^{-1}$. Both the stock solutions of TMB, bromate, and hypochlorite were stored at 4 ^{o}C.

UV/vis absorption spectra were recorded with a Cary 50 UV/vis spectrophotometer (Varian). Photographs were taken with a commercial digital camera. 96-well microplate was read with a EL-808 Ultra Microplate Reader (Bio-TEK).

1.2. Procedure for the bromate detection

Various volumes of ultrapure water were added successively with 10 μL of stock TMB solution and 20 μL of concentrated HCl (12 M). Then different volumes of bromate corresponding to a range of concentrations were spiked, with the final volume of solution equal to 200 μL. After homogeneous mixing, it stood for 10 min before the spectral recording.

1.3. Procedure for the hypochlorite detection

Likewise, various volumes of ultrapure water were added successively with 10 μL of stock TMB solution and 10 μL of diluted HCl (0.75 M). Then different volumes of hypochlorite corresponding to a range of concentrations were spiked, with the final volume of solution equal to 200 μL. After homogeneous mixing, it stood for 10 min before the spectral recording.

1.4. Procedure for the interference test on the bromate detection

120 μL of ultrapure waters were added with successively with 10 μL of stock TMB solution, 50 μL of standard bromate solution (1 μM), and 10 μL of standard solutions of other tested ions (10 mM). Then 20 μL of concentrated HCl (12 M) was spiked to all solutions, which stood for 10 min before the spectral recording.

1.5. Procedure for the interference test on the hypochlorite detection

Likewise, 160 μL of ultrapure waters were added with successively with 10 μL of stock TMB solution, 10 μL of standard hypochlorite solution (0.1 mM), and 10 μL of standard solutions of other tested ions (10 mM). Then 10 μL of diluted HCl (0.75 M) was spiked to all solutions, which stood for 10 min before the spectral recording.

1.6. The bromate assay of water samples

Three kinds of water samples, i.e. commercially bottled mineral water, groundwater, and cooled boiled tap water, were subject to no pre-treatment before analysis. Typically, 120 μL of ultrapure

water was added with 10 µL of stock TMB solution and 20 µL of concentrated HCl (12 M). Then 50 µL of each water sample was spiked. To be control, 170 µL of ultrapure water was added with 10 µL of stock TMB solution and 20 µL of concentrated HCl (12 M). For the standard addition, double 120 µL of ultrapure water were both added with 10 µL of stock TMB solution and 20 µL of concentrated HCl (12 M). Then 40 and 30 µL of each water sample coupled with 10 and 20 µL of standard bromate solution (5 µM) were spiked. All the solutions prepared doubly and stood for 10 min before the spectral recording.

1.7. The hypochlorite assay of water samples

Here the water samples were commercially bottled mineral water, purified drinking water, and tap water, respectively. Likewise, they were tested with no pre-treatment. In a similar manner, 130 µL of ultrapure water was added with 10 µL of stock TMB solution and 10 µL of diluted HCl (0.75 M). Then 50 µL of each water sample was spiked. To be control, 180 µL of ultrapure water was added with 10 µL of stock TMB solution and 10 µL of diluted HCl (0.75 M). For the standard addition, double 130 µL of ultrapure water were both added with 10 µL of stock TMB solution and 10 µL of diluted HCl (0.75 M). Then 40 and 30 µL of each water sample coupled with 10 and 20 µL of standard hypochlorite solution (20 µM) were spiked. All the solutions prepared doubly and stood for 10 min before the spectral recording.

2. Supplementary figures

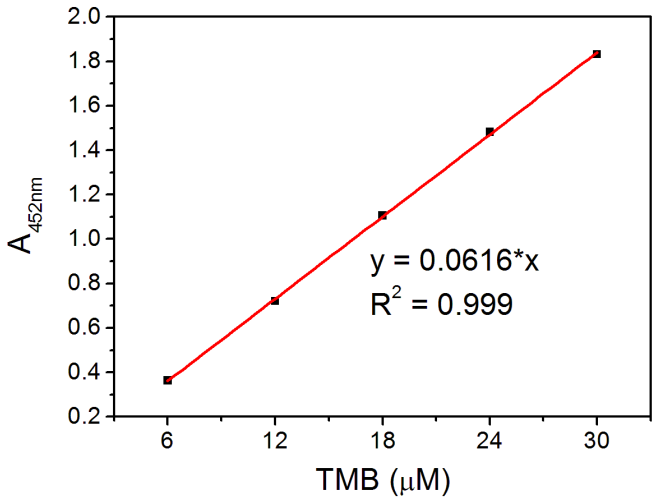

Fig. S1 Correlation of the maximum absorbance at 452 nm with TMB concentration after the complete oxidation of TMB with bromate in concentrated HCl acid.

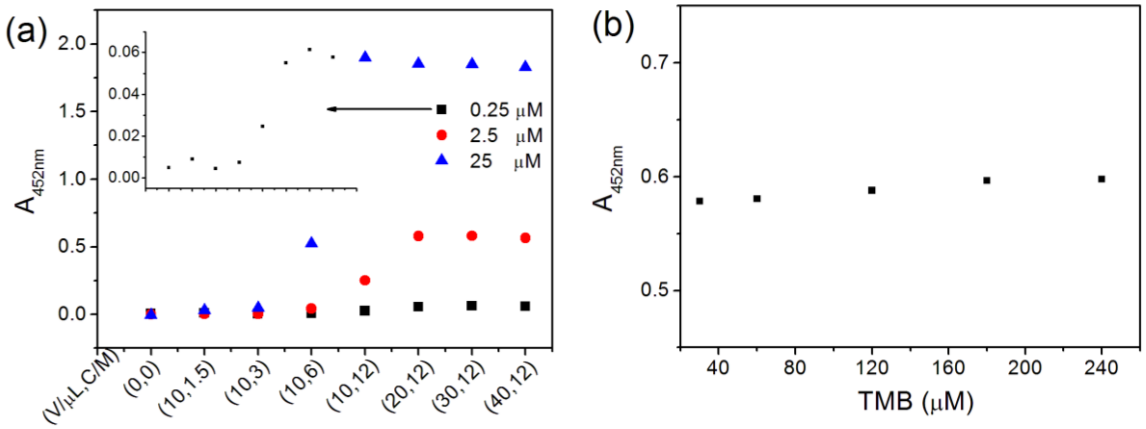

Fig. S2 Effect of (a) HCl concentration and (b) TMB concentration on the oxidation of TMB by bromate. For (a), TMB was 30 μM, and for (b), bromate was 2.5 μM and HCl was 1.2 M.

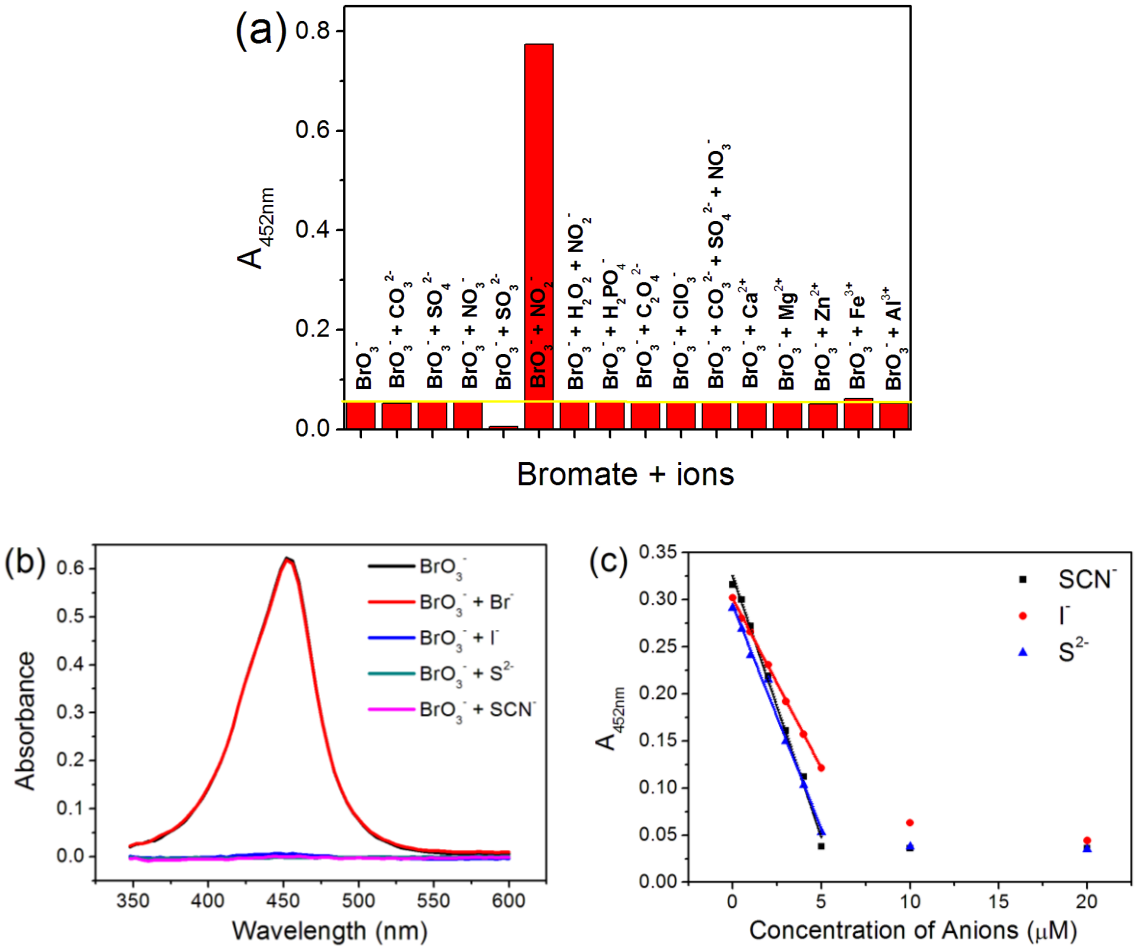

Fig. S3 (a) Interference test of the determination of bromate (0.25 μM) by the addition of other ions (0.5 mM). To remove the interference from nitrite, the addition of H_2O_2 to convert nitrite through peroxynitrous acid to nitrate was adopted. To implement this, H_2O_2 was first added to the solution containing bromate and nitrite, and then concentrated HCl acid was added. About 2 min later, TMB was added. The concentration of HCl and H_2O_2 was 1.2 M and 1 mM, respectively. (b) Interference test of the determination of bromate (2.5 μM) by the addition of bromide, iodide, sulfide, and thiocyanate ions (0.5 mM). (c) Inhibition study of the oxidation of TMB by bromate with iodide, sulfide, and thiocyanate, using 96-well microplate for the absorbance measurement. It can be seen the inhibition effect of sulfide and thiocyanate is more profound than iodide, evident from the larger slopes of variation for sulfide and thiocyanate.

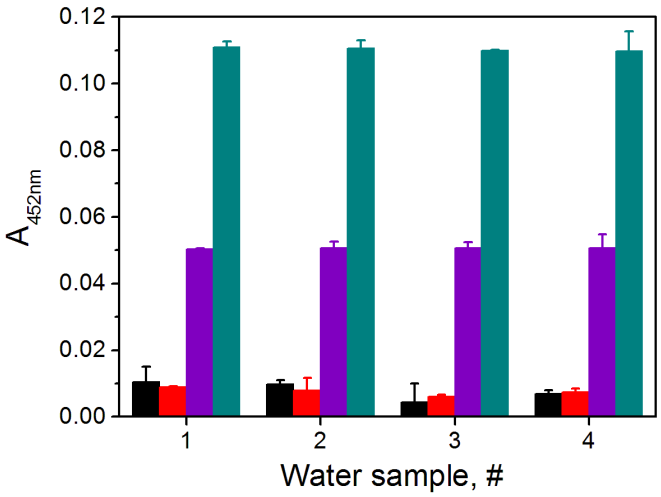

Fig. S4 Application of the TMB sensor solution in the determination of bromate in three water samples. The error bars represent the standard deviation of three measurements. Sample #1 and 2 were commercially bottle mineral water, sample #3 was groundwater, and sample #4 was cooled boiled tap water. The black column represents the control without the addition of sample and bromate; the red column represents the addition of sample; and the blue and green columns represent the addition of sample and bromate in different concentration. For more information, please refer to the Experimental Section (**1.6**).

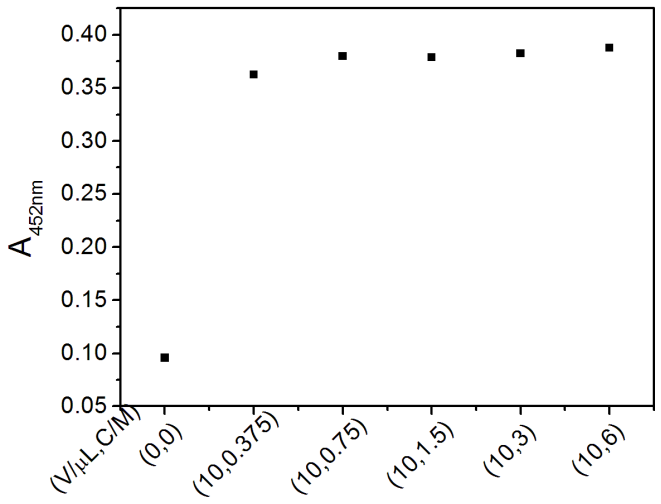

Fig. S5 Effect of HCl concentration on the oxidation of TMB (30 μM) by hypochlorite (5 μM).

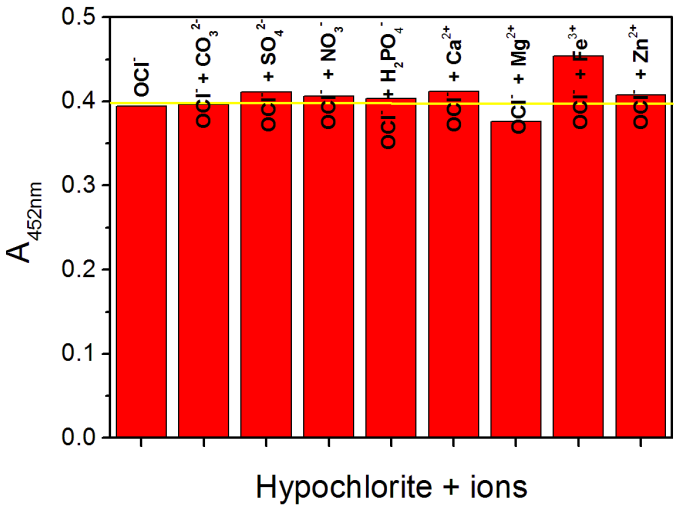

Fig. S6 Interference test of the determination of hypochlorite (5 μM) by the addition of other compatible ions (0.5 mM).

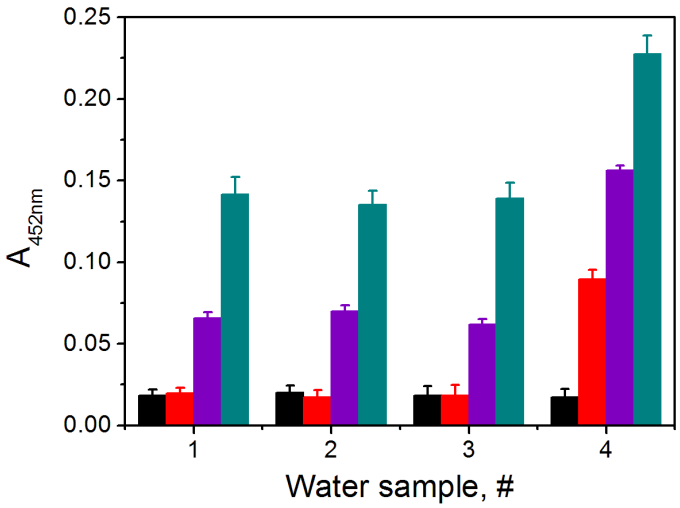

Fig. S7 Application of the TMB sensor solution in the determination of hypochlorite in three water samples. The error bars represent the standard deviation of three measurements. Sample #1 and 2 were commercially bottle mineral water, sample #3 was purified drinking water, and sample #4 was tap water. The black column represents the control without the addition of sample and hypochlorite; the red column represents the addition of sample; and the blue and green columns represent the addition of sample and hypochlorite in different concentration. For more information, please refer to the Experimental Section (**1.7**).

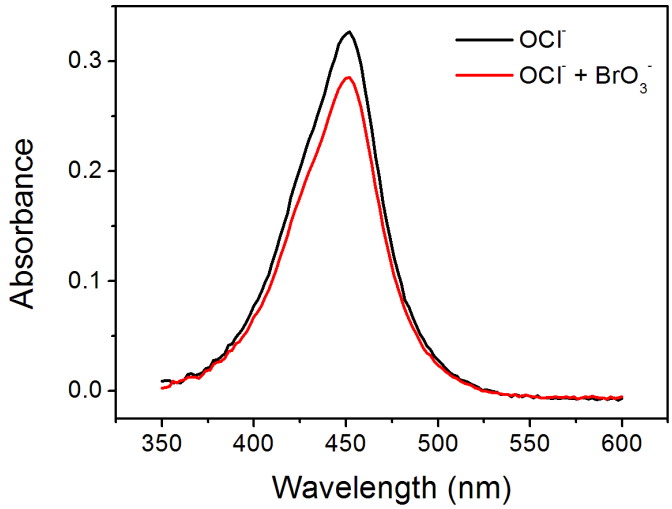

Fig. S8 Interference test of bromate (0.5 μM) in the determination of hypochlorite (4 μM). The concentration of HCl acid was 37.5 mM.

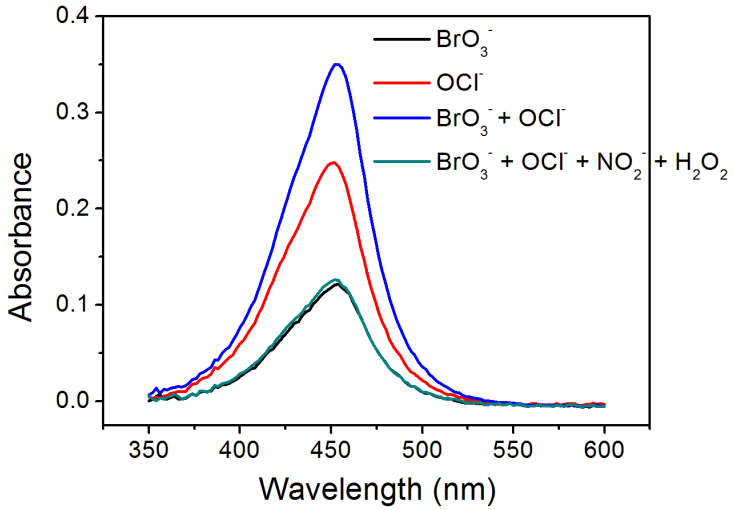

Fig. S9 Application of spiking nitrite and H_2O_2 to remove interference from hypochlorite in the determination of bromate. To implement this, excessive nitrite was first added to the solution containing bromate and hypochlorite, reacted with hypochlorite for about 5 min, and then H_2O_2 and concentrated HCl acid were added in sequence to convert excessive nitrite to nitrate as mentioned above (see Fig. S3a). About 2 min later, TMB was added. The concentrations of HCl and H_2O_2 were 1.2 M and 0.5 mM, respectively. The concentrations of bromate, hypochlorite, and nitrite were 0.5 μM, 4 μM, and 50 μM, respectively.

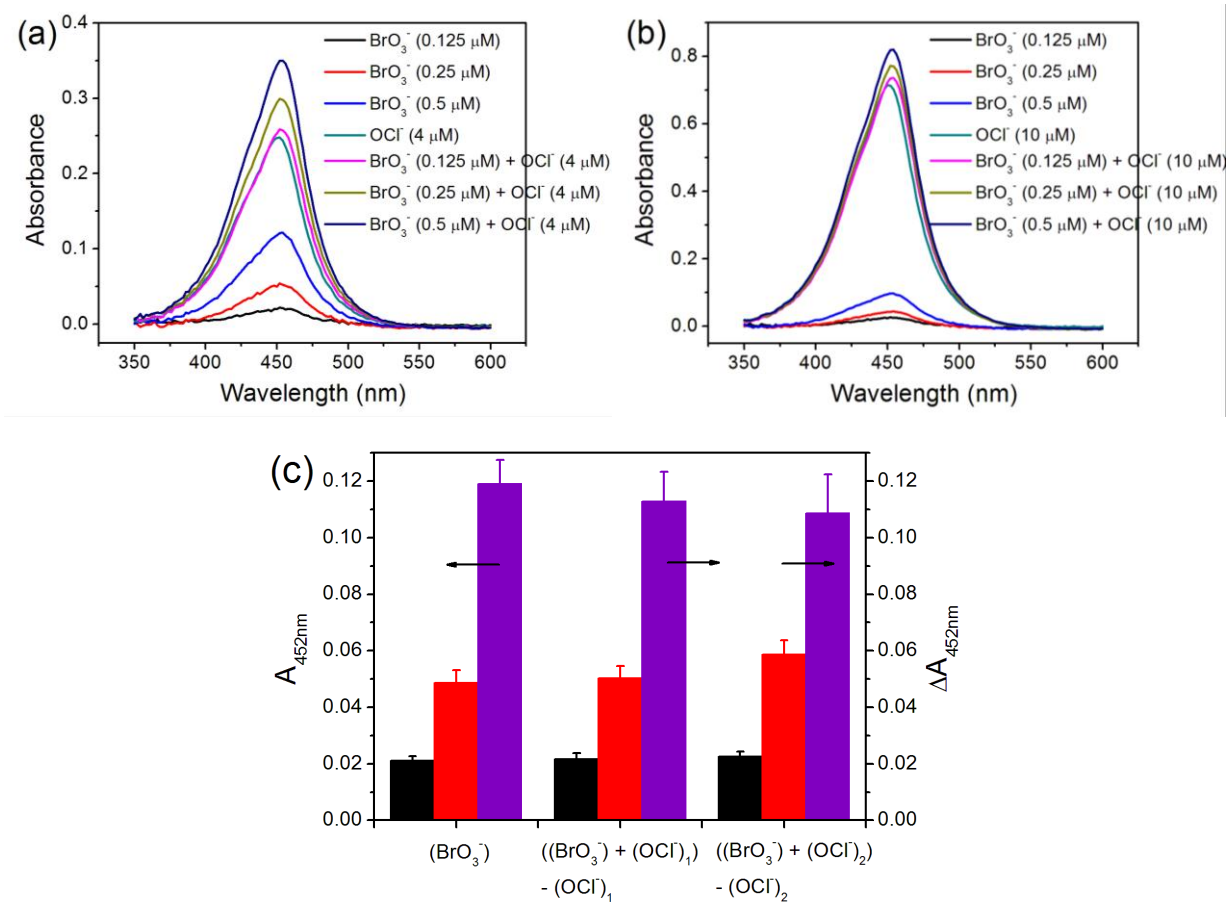

Fig. S10 (a, b) The optical spectra in the determination of different concentrations of bromate, one concentration of hypochlorite, and different concentrations of bromate plus hypochlorite. (c) Comparison of the absorbance at 452 nm for the optical spectra with respect to single bromate assay and the net absorbance at 452 nm through subtraction of the absorbance at 452 nm for hypochlorite by those for combined bromate and hypochlorite. In the determination of bromate and bromate plus hypochlorite, the concentration of HCl acid was 1.2 M, and in the determination of hypochlorite, the concentration of HCl acid was 37.5 mM. The concentrations of $(OCl^-)_1$ and $(OCl^-)_2$ were 4 μM and 10 μM, respectively. It can be seen that the net absorbance has insignificant difference from the absorbance for single bromate assay, no matter what the concentration of hypochlorite, suggesting that this absorbance subtraction method can be applied for the bromate assay when hypochlorite is present.