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Analysis of the oxidation of sulfur species of iron sulfides with dissolved oxygen☆

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Abstract:
This paper presents the results of a theoretical analysis of the oxidation processes of S^{2-} (equivalent to sulfur in iron monosulfides) and, respectively, of S_2^{2-} (equivalent to sulfur in iron disulfides) with dissolved oxygen. The analysis was performed using the Geochemist's Workbench software and it was found that in the presence of dissolved oxygen the main oxidation products of S^{2-} are S_2^{2-}, S_4^{2-} and sulfate. In the presence of dissolved O_2, it was found that the oxidation products of S_2^{2-} are S_3^{2-}, S_4^{2-} and SO_4^{2-}.

Keywords: S^{2-}, S_2^{2-}, O_2, pH, oxidation products

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1. INTRODUCTION

There are two major categories of iron sulfides, iron monosulfides (FeS) and iron disulfides (FeS_2). In the category of iron monosulfides we find minerals such as pyrrhotite, troilite or mackinawite [1-7]. In the category of iron disulfides we have pyrite and marcasite [7-9].

The sulfur in iron monosulfides has the -II oxidation state, and the sulfur in iron disulfides has the -I oxidation state. In the presence of oxidants, sulfur -II can transfer up eight electrons and produce various sulfur species, such as S_2^{2-}, S_3^{2-}, S_4^{2-}, S(0), SO_3^{2-} or SO_4^{2-} [1,2,7].

Upon oxidation, sulfur in iron disulfides can lose up to seven electrons and transform into S_3^{2-}, S_4^{2-}, S(0), SO_3^{2-} or SO_4^{2-} [7,8]. The formation of the SO_4^{2-} species cannot be achieved in a single step, because no more than two electrons can be transferred in an elementary reaction [10]. Therefore, it is expected that a series of species will be formed as reaction intermediates. The precise identification of reaction products and reaction intermediates, respectively, is difficult to achieve, because for kinetic reasons, reaction products can coexist with reaction intermediates [1,3,8,9].

The objective of this study is to establish as precisely as possible which oxidation products of S^{2-} and, respectively, of S_2^{2-} are stable in aqueous media at various pH values and at different oxygen activities.

2. METHODS

Stability calculations were performed with The Geochemist's Workbench® Community Edition software. Stability of the S^{2-} and S_2^{2-} species was investigated in the presence of dissolved oxygen (O_2) in aqueous medium, at 25 °C and a pressure of 1,013 barrs. The results obtained are presented in the form of stability diagrams.

3. RESULTS AND DISCUSSION

Figure 1 shows the stability diagrams of the S^{2-} (a=10^{-3}) and S_2^{2-} (a=10^{-3}) species in the presence of dissolved oxygen at 25 °C. As can be seen in Figure 1a, in the presence of dissolved oxygen, S^{2-} is not stable and can transform into S_2^{2-}, in acidic environments and low dissolved oxygen activities ($\log O_2 < -15$). At high values of O_2 activity, the stable species is S_4^{2-}, at pH < 10, and, respectively, SO_4^{2-}, in basic medium. The S_2^{2-} ion can transform into S_3^{2-} at low values of O_2 activity ($\log O_2 < -10$), regardless of pH (Figure 1b). At high values of dissolved O_2, the stable species at pH < 10 is S_4^{2-} and, respectively, SO_4^{2-} in basic medium.

If the concentration of the sulfur species (S^{2-} or S_2^{2-}) changes, the pH and oxygen activity limits at which each oxidation product is present change, but the oxidation products themselves do not change (Figure 2).

The stability calculations performed show that the most likely oxidation products of S^{2-} and S_2^{2-} are species in oxidation states lower than zero (at low oxygen activities) and, respectively, species in the maximum oxidation state (+VI) at high oxygen activities.

Species in intermediate oxidation states can in principle only be reaction intermediates. Not even S(0) appears to be a final oxidation product.

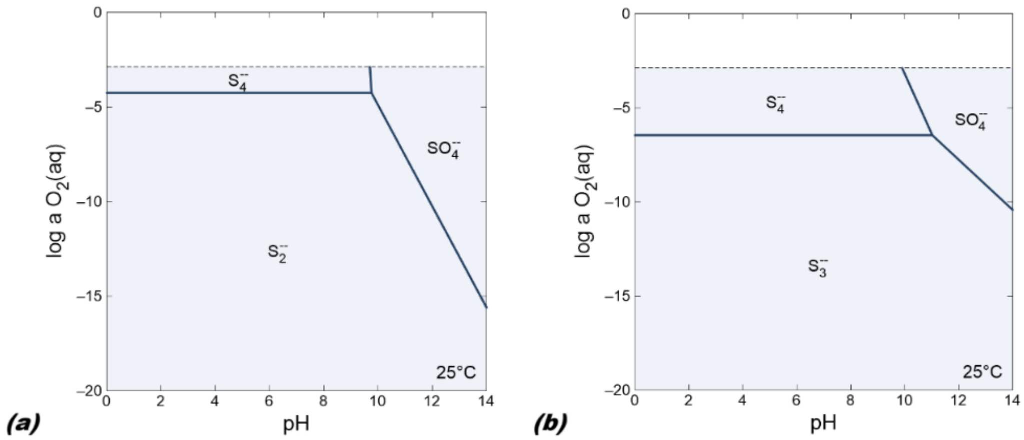

Figure 1. Diagram for (a) S^{2-} (a=10^{-3}) in aqueous solution and (b) S_2^{2-} (a=10^{-3}) in aqueous solution. The temperature is 25 °C, a_{H2O}=1, and the pressure is 1.013 barrs.

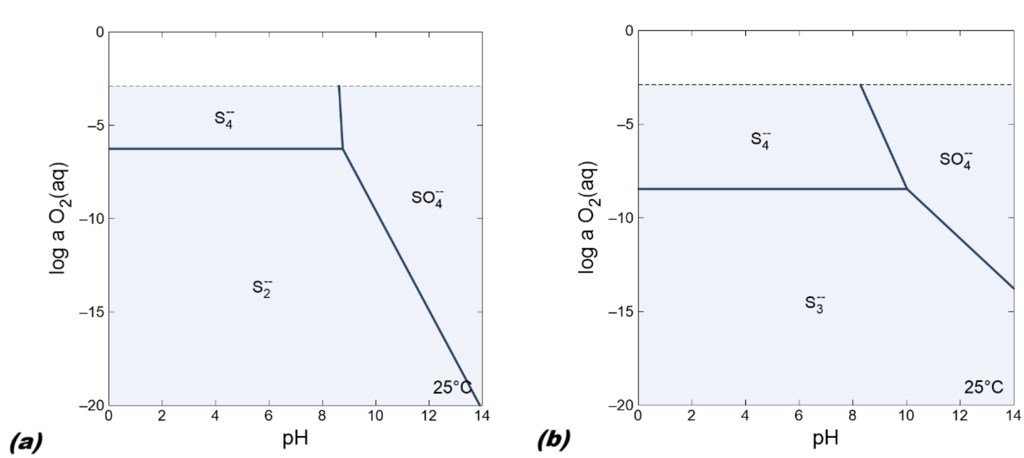

Figure 2. Diagram for (a) S^{2-} (a=10^{-5}) in aqueous solution and (b) S_2^{2-} (a=10^{-5}) in aqueous solution. The temperature is 25 °C, a_{H2O}=1, and the pressure is 1.013 barrs.

It is reasonable to accept that these results can be successfully used in the characterization of the oxidation of iron monosulfides and, respectively, iron disulfides, especially when the interaction between iron sulfide and the oxidizing medium involves the prior dissolution of the two species, S^{2-} and, respectively, S_2^{2-}.

The results of such an analysis may also be useful for other sulfide minerals, such as sphalerite (ZnS) or galena (PbS).

4. CONCLUSION

From the analysis of the stability of S^{2-} and S_2^{2-} species in the presence of dissolved oxygen, the following conclusions can be drawn:

- ✓ In the presence of dissolved oxygen, the main species that are stable in the case of the S^{2-} species are S_2^{2-}, S_3^{2-} and SO_4^{2-}.
- ✓ In the presence of dissolved oxygen, the main species that are stable in the case of the S_2^{2-} species are S_2^{2-}, S_4^{2-} and SO_4^{2-}.
- ✓ The behavior of the two anions in aqueous medium at various pH and oxygen activity values can reasonably

model the behavior of iron monosulfides and iron disulfides in the same type of medium.

- ✓ Such an analysis can be extended to other mineral sulfides, such as ZnS or PbS.

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