

Response

Response to the Comment by G. Druschel and M. Borda on “Pyrite dissolution in acidic media”

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Most of the seven sections developed in the Comment are actually generalities which, when related to our study, support our interpretations and conclusions. The Comment essentially accepts our experimental data but proposes a more consistent representation that redefines our results in the context of more complex pathways for pyrite oxidation. Only four sections (3, 5, 6 and 7) criticize explicitly our interpretations or conclusions. We will focus on these criticisms.

The authors of the Comment first challenge the set of reactions through which we proposed to interpret our experimental results. Our set of reactions would be poorly consistent with the chemical reactivity of thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$), the two intermediary species we proposed. Previous studies on pyrite oxidation at acid pH failed to detect or to measure quantitatively elemental S or metastable sulfoxyanions in solution, as has been noted by the Comment's authors. This implies that electron transfer is very rapid at low pH. However, the non-congruence of the dissolution reaction observed in our study, among others, suggests that intermediary species must be removed from the solution as precipitates or as gases. That means that the lifetime of intermediary species, or their occurrence in solution, remain as key questions, despite the generalization that some species, such as $S_4O_6^{2-}$, can be considered relatively stable in solution (but only in absence of pyrite or at higher concentrations). This was extensively discussed in our paper.

The authors of the Comment assert that if tetrathionate ion was an actual intermediary species in our study, we should have detected it, since they studied its stability.

Unfortunately, their experimental conditions are different from those of our study: they used higher concentrations of tetrathionate, namely from 120 up to 2000 μM , while in our study we estimated it was always less than 10 μM (if we consider run M22). Moreover, they always used excesses of ferric Fe (from 0.5 to 10 mM), while in our study we estimated it was always less than 10 μM (if we consider run M21).

The authors of the Comment assert that $S_2O_3^{2-}$ is stabilized by Fe^{3+} as a result of the formation of Complex $FeS_2O_3^+$. Again, this is valid only in the chemical conditions where it has been observed: $FeS_2O_3^+$ dissociates at the low concentrations we used, as it can be calculated from the stability constant reported by Williamson and Rimstidt (1991) (a publication cited by the authors of the Comment) and from Mahapatra et al., 1957, *i.e.*, $\ln K = 2.1$. $FeS_2O_3^+$ dissociates when its concentration is less than $10^{-2.1}$ M, and in our study we estimated both S and Fe concentrations were less than 10^{-6} M.

The authors of the Comment seem to agree that $S_2O_3^{2-}$ is an intermediary species, but they propose it is always attached to the surface, while we would have put it in the aqueous solution. This is an interesting point: we actually do not know whether or not this intermediary species was still attached on the surface. Despite what the authors of the Comment state, both situations can be accommodated in our interpretation. Indeed, in our interpretation we determined the oxidation numbers of two intermediary species from $R = 2n/n'$ (Eq. (11)), where n and n' are, respectively, their oxidation numbers, and R is the experimentally measured ratio S/Fe in the course of the dissolution. Our model calculation of R essentially relies on charge balance: by definition, charge balance and oxidation numbers of species are the same wherever the species are typi-

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cally attached to the surface or in aqueous solution. For this reason, assuming that the intermediary species $S_2O_3^{2-}$ is at the surface does not contradict our conclusions or interpretation. However, disproportion might need two reactants, which might very well require that at least one of them is in the solution. We did not discuss this point in our publication, since we do not have any strong experimental evidence for deciding where the intermediary species were. We only inferred non-congruent dissolution (along with others) and oxidation states of intermediary species.

In response to another direct criticism, we did intend to detect elemental S by using several techniques such as XPS, nuclear microprobe, or observations of filtrates by SEM (see the specific section in our paper). As we wrote: “*We can possibly explain this [the failure to detect S^0 precipitates at the pyrite surface] by the small amounts of matter involved. In the case of the M21 experiment, if we considered the total amount of S based on Fe concentrations, S^0 in colloidal form would represent $1.8 \times 10^{-6} \text{ mol L}^{-1}$ at the end of the run, i.e., 32 ppm. Our estimated XPS detection limit is 1000 ppm. Also, elementary S under vacuum conditions is volatile and tends to sublime even at 270 K (Mycroft et al., 1990).*” Elemental S was observed at low pH in others studies when ferric Fe is added in excess (Sasaki et al., 1995; Schippers et al., 1996; McGuire et al., 2001), which is far from our experimental conditions. However, we agree that more specific and on-line techniques (e.g., reversed-phase chromatography or extraction of S with solvents followed by liquid chromatography or Raman spectroscopy) dedicated to measure elementary S at very low concentrations, as in our experimental conditions, should be used in further studies.

Besides the disproportion of $S_2O_3^{2-}$ into $S_4O_6^{2-}$ and S^0 , we proposed in our previous paper an additional and possible degassing of SO_2 to explain the decrease of the $[SO_4^{2-}]/[Fe]_{\text{tot}}$ ratio at very low pH. We did not intend to directly measure such degassing, since in our experimental conditions S concentrations would have led to very small amounts of SO_2 . We share the authors’ opinion and suggest the use of specific equipment, such

as gas chromatography, to verify this assumption in future work.

The authors found some “rigidity” in our model, because they believe we would describe all of the reaction products as a consequence of one, and only one, set of sequential reactions, which must then be consistent over the applicable range of conditions. Our goal was to describe more completely the aqueous oxidation products of pyrite, without ignoring surface observations. In acidic solution and in the presence of pyrite, as intermediary reactions appeared to be too rapid to permit any quantification of sulfoxyanions, and as we did not find enough information from our XPS, nuclear microprobe, SEM or FTIR observations, we focused our interpretation on the relative constancy of the experimental R values. The results obtained and the interpretation of the R value allowed us to propose hypotheses concerning the mechanism of pyrite oxidation. These hypotheses are consistent with previous studies and even with the schema given by the authors of the Comment, when eliminating the numerous pathways corresponding to stoichiometric dissolution: only Path 1A leads to a non-stoichiometric dissolution. This path is quiet similar to the one we proposed, and was already checked in our paper. In this case, the R value would not be equal to 1.6, but 1.0.

We are aware that the mechanism of pyrite oxidation is complex, and as we said in our paper, further investigations must be performed to validate completely our model. Lastly, our model can take into account all the previous studies providing enough information for calculating R . Conversely, among all the reactions they suggested, the Comment’s authors did not particularly attempt to select those reactions consistent with experimental R values in acidic media.

Reference

- Mahapatra, G., Nanda, C., Patnaik, D., 1957. Spectrophotometric study of the ferric thiosulfate complex. Part III. *J. Ind. Chem. Soc.* **34**, 458–460.