    Reviewer: 3  
  
    Comments:  
    no further comments, revision well done  
  
  
    Reviewer: 2  
  
    Comments:  
    This paper describes experimental Ra adsorption to different minerals under different pH conditions. As much as the authors have addressed some the comments I made for the first round of the revision, there is still a fundamental question of how much this paper makes a different in our understanding of the factors that control Ra adsorption. Unfortunately, I see only partial improvement, specifically with respect to the chemistry of SGD.

With respect to hydraulic fracturing operations, the authors totally missed the point; first they do not explain why that brines in reducing conditions with clearly presence of pyrite minerals in shale formations are so much enriched in Ra and thus the large Ra adsorption they describe in their experiments seems not to apply to the real-world conditions, or have negligible effects relative to other factors.

[RESPONSE]: In figure 1, we demonstrate that in spite of Ra having high sorption to pyrite normalized to surface area, only a fraction of the Ra available in solution was able to sorb to the pyrite surface. This effect is further shown in figure 2, where only a maximum of ~20% Ra sorption to pyrite is shown over various geochemical conditions considered. Thus, in a typical fracturing shale, which have had geologic time scales to reach secular and chemical equilibrium, it is not surprising that Ra remains in solution. The highly complex geology and chemistry of shale brines also may interfere with pyrite sorption to Ra. However, pyrite has not been previously considered as a potential sorptive phase for Ra, and this study presents evidence that further research is needed to constrain how pyrite phases may impact Ra retention and release during hydraulic fracturing. We have updated the manuscript to emphasize these points in lines 365-371.

Second, they addressed the injection of hydraulic fracturing fluids, which typically occurs through deep-well injection that have no environmental impact. Instead the release of Ra-rich hydraulic fracturing fluids/wastewater to the environment through spills and disposal from treatment plants has major environmental effects and the retention of Ra on solids associated with spills and wastewater discharge is a major issue that needs consideration. Unfortunately, this study does not address this point.

[RESPONSE]: The chemistry of produced waters released during hydraulic fracturing is intimately connected to the interaction of fracturing fluid with the target formation and associated brines. Indeed, that Ra isotopes ratios have been highlighted as formation specific markers for contamination highlights this coupled nature as discussed in lines 298-304, the associated references, and 350-354 of the new manuscript. We have specifically updated the manuscript to directly address this point, however, in lines 357-362 of the new manuscript  
  
    Overall, I suggest to the authors to fully address the points I raised in my first evaluation. You should include the Ca/Na ratio variations in the solutions to demonstrate the specific role and the thresholds from which Ca over Na affects Ra adsorption – this is really critical for understanding the adsorption mechanism with clear implications for the real world cases.

[RESPONSE]: We agree with the reviewer that further understanding of Ra geochemistry will indeed require finding limits over which specific cations will control Ra sorption. We do not agree however, that Ca/Na ratios would sufficiently provide this understanding. Figure 2 of the manuscript demonstrates how even cations from the same group have clear, differential impact on Ra sorption to the minerals studied here. For example, Na and K show differential sorption, thus the ratio of both Ca/Na and Ca/K may be important. This differential sorption is found for all of the cations studied here, and a study examining the limits of cation influence on Ra sorption would require a comprehensive study where the various cation ratios are carefully varied alongside pH and sorbents. This would be beyond the scope of the study here, whose objective was to provide initial insight into the potential geochemical conditions, as discussed in lines 88-94 of the manuscript, given the limited understanding that has been developed so far, as discussed in lines 66-83.

Also, you should further explain how the experimental results of this study help to understand other cases, beside SGD, where Ra-rich fluids interact with solids (e.g., under anoxic condition such as shale formations and under oxidizing conditions such as disposal of produced water to rivers and soil).

[RESPONSE]: See above replies to comments. We address the potential impacts for hydraulic fracturing in lines 350-378 of the updated manuscript, as well as how the results of the study point to potential methods of mitigating the release of Ra to the environment from hydraulic fracturing, by tuning hydraulic fracturing fluids to enhance Ra sorption during injection.  
  
    Given that surface complexation modeling conducted in this study does not really help to predict the impacts of different geochemical conditions on Ra adsorption, the only real contribution of this study is that Ra can be adsorbed onto other minerals, particularly to pyrite.

[RESPONSE]: This study provides multiple contributions beyond simply the indication that Ra adsorbs minerals such as pyrite. The first is that it systematically examines how Ra competes with different potential background cations, which has not been done for Sodium Montmorillonite, and has not been done for many common cations onto the iron (hydr)oxides (Ex. Mg, K etc.). The second is that this work clearly delineates that sorption is highly differential among mineral phases, and that common trends (ie iron oxides highly sorb Ra) can be reversed by changing geochemical conditions (pH, competing cations). Lastly, the surface complexation modeling provides some limited insight into the Ra sorption mechanism. For example, SCM of the sorption envelope to the sodium montmorillonite required both a cation exchange component, and a surface sorption component, while SCM of Ra sorption to iron (hydr)oxides did not require this. While models did not correctly predict the impact of alternative sorbing cations on Ra sorption, this could have been driven by the missing or incomplete information available for sorption of those cations to their respective mineral phases. These are discussed in the final paragraph of the manuscript, lines 379-389.

This again, contradicts field observations that show high Ra in reducing environments where pyrite present does not seem to have any major impact on Ra retention. I would encourage the authors to resolve this apparent contradiction to make this paper publishable in ES&T.  
  
  
[Alternative Response]: The reviewer raises a few points of clarification that we believe will help illustrate the implications of the Ra study we have performed here, and we have made some alterations reflecting those clarifications.

The first is the apparent contradiction between observed Ra in natural waters (subterranean groundwater or shale formation brines) and the results of our study that show pyrite can sorb significant amounts of Ra. We discuss this in context of estuarine waters in lines 327-337, and in the context of deep shale formations in lines 363-371. In short, while sorption was observed to pyrite surfaces, no sorption experiment including pyrite studied showed complete sorption of experimental Ra. Thus, no contradiction exists, as even in the case where geochemical conditions favor Ra sorption to pyrite, some will still remain in the supernatant. Indeed, for conditions that are representative of natural groundwaters (figure 2, 10 mM ionic strength mixed cation background solution), complete sorption of Ra was not observed.

The second point the reviewer raises deals with addressing how our results impact additional scenarios where Ra may pose a human health hazard, particularly with respect to hydraulic fracturing. While injected fluids may not contain Ra (though many do, since they are recycled from previous operations), the mixing of the injected fluids and formation brines lead to the Ra content observed in produced water. We discuss this linking in lines 298-304, as well as lines 354-362 and lines 371-376 of the updated manuscript. Additionally, this linkage points at the possibility of engineering hydraulic fracturing injections to reduce Ra load in produced water, which would reduce possible contamination risks during fluid handling. Lines 354-362 in particular address these contamination risks and discuss how the disparity between produced water and local groundwater would likely result in additional Ra retention by shallow aquifers.

Third, the reviewer requests that we analyze the impact of Ca/Na ratio on Ra sorption to the mineral phases studied here. While we agree that additional work investigating the impact of these different ions is necessary to constrain Ra sorption, we disagree with the reviewer’s assertion that this ratio alone would elucidate the mechanisms controlling Ra sorption. Figure 2 of this manuscript clearly highlights how even in single cation background solutions, stark differences in Ra sorption appear depending on the background cation. Based on this, studying the geochemistry of Ra would thus require a comprehensive experimental study, where multiple ratios of background cations and Ra are examined. At minimum, such a study would need to quantify the impact of Ca/Na, K/Na, and Mg/Na, but addressing the reviewer’s request here would likely require comparison other ratios, as well as the impact of mixtures of these background cations. This is beyond the scope of the work laid out in lines 84-94 of the manuscript.

Lastly, the reviewer states that the only novel contribution of this work is the data regarding Ra sorption to pyrite, given the failure of the SCM used here to predict the impact of different geochemical conditions. We disagree with this statement. While the literature does contain some work constraining the impact of specific cations as noted lines 67-78 and the associated references, the matrix of geochemical conditions (pH, ionic strength, background cation composition) and mineral phases studied here has not been previously addressed. Additionally, while the SCM used here lacks full predictive capability, the models were able to illustrate key mechanisms at play in Ra sorption. For example, Sodium Montmorillonite SCM required the inclusion of cation exchange, a mostly pH independent mechanism as compared surface site sorption seen in the (iron)hydroxides. We argue, therefore, that the work here provides key initial insights into the complex geochemistry of Ra.

    Reviewer: 1  
  
    Comments:  
    I have read through the authors' response to reviewer comments and the revised manuscript, and have no further comments. I support publication of the paper in its current form.