Review of "Synchrotron-based elemental mapping of single grains to investigate variable infrared-radiofluorescence emissions for luminescence dating"

This is an interesting work in which authors tried to identify the causes in variation in shapes of the IR-RF curves and attributed them to variations in elemental concentrations inside mineral grains. The authors also conclude such variations can result in wrong estimation of doses. Although methodology adopted seems reasonable, there are still several scientific aspects, which are not clear and need to be addressed.

Comments:

1. Page 2 line 38, Introduction: "rely on the capacity of". Its not capacity, its property of defects. Change appropriately.
2. Page 2 line 40, 41, Introduction: "In the laboratory, the total amount of energy stored" and "energy absorption rate (dose rate, Gy a-1)". Energy per unit mass is dose.
3. Page 2 line 43, Introduction: "quartz because of its high abundance and resistance to weathering". Besides these two, the fast to bleach OSL signal makes it most appropriate for geological dating.
4. Page 2 line 45, Introduction: "considering a low dose rate of 1 Gy ka-1"
5. Why to mention 'low' here? Please delete low
6. Page 2 line 64, Introduction: "saturation cap at around 1500 Gy, reducing" cap can be deleted
7. Page 3 line 80, Method rationale: "study, between one and three grains (~…….. curves"
    Statement not clear, consider revising.
    What is the reason for bad match? Bad match is often observed due to sensitivity changes. Pls refer (Varma, V., Biswas, R.H., Singhvi, A.K., 2013. Aspects of Infrared Radioluminescence dosimetry in K-feldspar. Geochronometria 40, 266-273.)
8. Page 3 line 83, Method rationale: "grains that emitted a detectable signal displayed the expected decay shape." What is meaning of expected shape here? exponential decay?
9. Page 3 line 89, Method rationale: "With dose exposure, the 955 nm emission increases and overlaps with the 880 nm peak." Why is it so? How dose increases the 955 nm emission, does it mean more 955nm recombination centres are being regenerated? Does it reflect multiple trap system?
10. Page 4 line 101, Method rationale: "The thermal stability of the ~710 nm emission has been, however…. the measured IR-RF" The red TL emission in feldspar is generally considered more stable than conventional IRSL method, why the red IR-RF is unstable?
11. Page 4 line 111, Method rationale: "The µ-XRF and µ-XANES techniques are best suited for this purpose by producing high-resolution maps of elements and their oxidation states".
    It will be good to provide some details about the mentioned techniques and their usefulness for present work.
12. Page 3 line 83, Method rationale: "The use of synchrotron µXRF allows us to improve the spatial resolution compared with previous uses of µXRF (e.g., Buylaert et al., 2018) by reducing the beam spot size from ~25 µm to 1 or 0.5 µm"
     It is indeed impressive that spot size is smaller and we can work at higher resolutions, but how will it effect S/N ratio and thus elemental concentration estimation? In addition, since spot size is smaller, only few grains analysis may be possible. In such cases, how can we get the statistical representation of entire grain population just based on few grains studies?
13. Page 4 line 128, Material and instrumentation:

Normally Tuff samples are expected to contain Fe rich species. Is this a deliberate choice to look the effect of Fe in the samples as 2 out of 5 are tuff samples?

14. Page 5 line 134, Material and instrumentation: Why only the sample H22550 was etched with HF. Why not same is performed for other samples?

15. Page 5 line 134, Material and instrumentation: "Multi-grain and single-grains … National Laboratory"
How correspondence between IRRF and XRF signals is established?

16. Page 5 line 143, Material and instrumentation: "2016). Grains were fixed on a polymer microscope slide…………" What are spectral and luminescence characteristics of the base material used?

17. Page 5 line 144, Material and instrumentation: "XRF maps were obtained by scanning across pre-selected regions on the grains 90 x 90 μm maps," What is the basis of ROIs selection?

18. Page 5 line 149, Material and instrumentation: "resolution of 0.67 μm was achieved by focusing the beam with" Is it Xray beam focussing or luminescence focussing, please specify.

19. Page 5 line 150, Material and instrumentation: " An incident beam energy of 13.5 keV was" Why this energy chosen any specific reason?

20. Page 5 line 150, Material and instrumentation: "fluorescence was detected through the sum of 4 silicon drift detectors" Why these four detectors were used? Can we use PMT instead? whats the advantage we get with use of these detectors.
Can you provide geometry of measurements and experimental setup?

21. Page 5 line 152, Material and instrumentation: "All XRF measurements were normalised to the corresponding incident X-ray flux " X-ray sources are normally found inhomogenous spatially and temporally. Does this can effect your measurements?

22. Page 5 line 150, Material and instrumentation: "The XANES maps had a resolution of 0.5 μm (60 x 60μm)." Are units correct? How does 60 um X 60 um translate to 0.5um? not clear.

23. Page 5 line 150, Material and instrumentation: "we varied the incident beam energy according to the absorption edge values obtained from the μXANES measurements of Fe standards (Fe foil, pyrite, hematite)." How the specific absorption edge values were estimated?

24. Page 5 line 150, Material and instrumentation: "(i) the total Fe (at 7.275 keV)," The energies mentioned here are quite precise. How much is normally the resolution. Since electronic energy levels of specific elements are quite low in energy (~few eVs) compared to what is being provided, then why this much precision is needed?

25. Page 6 line 165, Results: "500 Gy succeeded by an increase, roughly following a saturating exponential shape" What is reason behind increase to saturating exponential behaviour? Why should there be an increase at all considering physics aspect? What is the nature of sample X7343, Is it similar to volcanic tuff?

26. Page 6 line 169, Results: "contamination, potentially coming from coating around the grains, we" Why is it assumed that coating could be responsible?

27. Page 6 line 171, Results: "Despite using density … high Fe content". Does that mean it is Na or Ca feldspar grains? Have you performed XRD analysis on bulk to see the mineralogy of samples?

28. Page 6 line 176, Results: "their visual appearance under a microscope" What were the visual indicators considered for choosing K-Feldspar?

29. Page 6 line 178, Results: "grains. The regenerated IR-RF signals showed a clear distinction between the two aliquots (Fig. 1), proving it is possible to separate the two observed IR-RF shapes." This is quite a qualitative way. I am not sure how to progress using only visually inspected grains. The visual appearance and selection can vary depending upon geological

settings of grains as well as person observing them. Is there any other rigorous way of making such selection?

30. Page 6 line 184, Results: "presumed to be the low-K, Fe rich minerals identified via SEM-EDS" Low K means possibly high Na or Ca, why only Fe is considered. Fe if present should be in form of defects, which should be in ppm level. Can uXRF measure to such low concentration levels? If Fe is appearing as major element in feldspar separates, it means it is present in stoichiometric formula and in that case, mineralogy of sample would be different. Please suggest if I am missing something.

31. Page 6 line 186, SG IR-RF characterisation: "signal of twenty-two individual grains coming" Can you specify mineralogy of each grains, which are picked for such measurements?

32. Page 6 line 165, SG IR-RF characterisation: "2): Category #1 for grains with a decreasing IR-RF signal, category #2 for grains with an increasing IR190 RF signal, and category #3 for grains with a flat signal". How many grains falls in each category and is there any link to the provenance.

33. Page 6 line 165, SG IR-RF characterisation: "we also observed the unwanted decreasing IR-RF signal for one of the four grains for sample H22550, which is from a coastal sand deposit." We expect IR-RF signal to decrease with irradiation, so why it is said unwanted ?

34. Page 6 line 193, SG IR-RF characterisation: "When the total signal of the theoretical aliquot was composed of more than 50% of signal from the category #2 grain, we observed the same decay shape as in figure 1 for a multi-grain aliquot sample X7343"
Obviously, since the two different category of grains having two different IR-RF characteristics are being added, so the result will depend on the proportion of the individual populations in the mixture. More importantly, it is important to know, how these two grains are different with respect to crystallography or stoichiometry or defects concentration. Is the nature of curve repeatable over repeated bleaching and irradiation cycles?

35. Page 7 line 201, SG IR-RF characterisation: As mentioned by authors, long-term signal stability may not be there for bad traps, is there a way to prove it? How do we know it without experiment?

36. Page 7 line 204, SG IR-RF characterisation: "Further, our results demonstrate…" I agree with this statement, but it is still not clear how can we segregate K-Feldspar and other minerals. Manually it will not be possible on routine basis.

37. Page 7 line 207, Subgrain µXRF elemental maps: "We then fitted each of the **18 225** spectra for…." this statement is not clear

38. Page 7 line 212, Subgrain µXRF elemental maps: "characterise visible inclusions (see Table 1)." The number of grains analysed per samples are quite small to represent the statistics of system. Can we consider them as representative of whole samples? It is difficult to conclude unless sufficient data points exists.

39. Page 7 line 214, Subgrain µXRF elemental maps: "all contain K, Pb, Fe and Ba, among other elements (Fig. 4)." What is typical concentration of these elements? Considering K is a major element present in stoichiometric formula, how much is relative concentration of the other elements?

40. Page 7 line 223, Subgrain µXRF elemental maps: "grains from category #3 cluster relatively close to those from category #2, suggesting"
How and why does this effect the IR-RF properties? These are observations, but what is the reason for IR-RF signal due to such clusters is not clear.

41. Page 7 line 237, Mapping oxidation states with µXANES: "suggest that Fe exists on the surface of this feldspar grain in its Fe^{3+} and Fe^{2+} states." It is great that using uXANES, we could map

the presence of Fe on the surface of feldspar grain, but luminescence or IR-RF is a volumetric phenomenon. How this observation is helpful in explaining the IR-RF signal.