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SHORT COMMUNICATION

Comments on the paper 'Mineralogical and geochemical analyses of the healing elements in clayey soils from Isinuka traditional spa in Port St Johns, South Africa'

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As a geologist with a pet interest in medical geology, my eye was immediately caught upon going through the table of contents of volume 68(1) of the *Transactions of the Royal Society of South Africa* by the paper by N.D. Jumbam, purporting to describe the mineralogical and geochemical composition of clay from the Isinuka Springs in Port St Johns. The first of many problems with the paper already became clear upon reading the abstract, which suggested that "The highest mean concentration of an element recorded was for Sr, with a mean value of 2550 ppm." Having some knowledge regarding the typical elements encountered in clay-rich materials, I immediately knew this to be untrue, so I assumed that what should have been said was that the highest mean concentration of an element forming part of the suite of trace elements analysed was 2550 ppm. However, upon inspection of Table 2, I did not know anymore what the author intended to convey, because the maximum concentration of Sr found in any of the samples analysed was 2118 ppm (in sample 8). Whilst on the topic of the contents of Table 2, let me turn to the two columns labelled SARM-4. I suppose that one of the columns represent the certified values for this reference material, and the other the values found for this reference material during the study that was performed. However, nowhere in the paper is it stated which column represents which. I also note that the Cr_2O_3 content in the left hand side column labelled SARM-4 is given as 30%, which is significantly different from that given in the right hand side column. The analytical total in the left hand side column is also significantly greater than 100%, which should not be the case if the analytical results are to be trusted. Furthermore, it is reported on page 27 that an amphibolite certified reference material was analysed during the study, whereas SARM-4 is a norite.

Clarification is also necessary concerning the gases emitted by the springs, since on page 26, the author makes mention of a "hydrogen sulphide-like odour" and on page 28 "a pungent sulphur dioxide-like smell". I have had the unfortunate privilege of smelling both of these gases myself, and their smells are quite distinct from each other. The nature of the gases emitted is obviously of some importance, as the former may point to quite reducing conditions and the latter to more oxidising conditions.

The section on materials and methods was also found to be woefully inadequate, with the reader being referred to an unpublished manual of the Council for Geosciences [*sic*] and a general text on analytical geochemistry. Nowhere in the former are the analytical conditions used for the X-ray diffraction and particle size analyses conducted as part of the study mentioned. Also, sulphur values are reported on page 28, but nowhere is it stated what technique was used for the determination of sulphur. It would appear as if sulphur was not analysed as part of the X-ray fluorescence analyses, because of the absence of the element from Table 2.

More questions arose upon reading the section on the particle size distributions of the samples due to the lack of a scale on both the vertical and horizontal axes on Figure 1. I was also surprised to learn that the chemical formula for the mineral chlorite was ClO_2, and by the blanket statement that "Quartz, mica and illite are very stable minerals." The diffractogram of sample 1, given as Figure 3, furthermore shows the presence of only 5 minerals, whereas Table 1 would lead the reader to believe that sample 1 contains no less than 11 minerals. It is also unfortunate that the x-axis of Figure 3 is given in 2θ units, especially so given the fact that the analytical conditions for the X-ray diffraction analyses are nowhere reported in the paper, leaving the reader incapable of using Bragg's law ($n\lambda=2d\sin\theta$) to convert peak positions to the mineralogically more useful d-values. From Figure 3, it appears as if the samples were scanned from ~5° to ~70° 2θ. Supposing the use of Cu Kα radiation for the X-ray diffraction analyses, I expected the development of a broad peak in Figure 3 at fairly low 2θ values (say at ~7–8°) if illite-smectite interstratification forms part of sample 1. This is clearly absent from Figure 3, yet the author suggests the presence of 10% illite-smectite interstratification in sample 1, according to Table 1.

Turning to the geochemistry of the analysed samples, the author suggests that hexavalent chromium (CrO_3) was not detected in the samples, whereas the less dangerous trivalent chromium (Cr_2O_3) was. How was the speciation of chromium in the samples determined? Could total chromium merely have been expressed as Cr_2O_3 as part of the X-ray fluorescence analyses or was the absence of hexavalent chromium determined in some other way?

At the bottom of page 29, I assumed that the use of "Ur" as a substitute for "U", which is the correct chemical symbol for the element uranium, represented a typographic error, yet the author chose to reuse the symbol "Ur" on a further two occasions. I also do not follow the author's arguments about

the potential health risks of radioactive Sr that is supposedly "risky when taken in, based on its carcinogenic and mutagenic mechanism." The last time I checked, Sr had four naturally occurring isotopes, all of which are stable. Am I missing something here? The author also states that Sr is "non-toxic when ingested at concentrations of 0.8–5 mg with food, when it only contains non-radioactive Sr." Firstly, milligram is not a unit of concentration, and secondly, where would potentially radioactive Sr come from in the case of the Isinuka springs? The author also suggests that radon was not detected in the samples. How was radon (a gas) analysed for? With X-ray fluorescence spectrometry?

The author furthermore suggests the presence of quicklime as a contributory factor to the alkaline nature of the samples. Quicklime is known to react violently with water to form calcium hydroxide. Seeing that the sediments analysed as part of the study all come from aqueous environments, how does the author explain the persistence of quicklime in the analysed samples? I also have serious problems with the author's contention that "The presence of TiO_2 and Zn in the samples is most likely responsible for protecting the skin of the users from ultra violet radiation." Whereas pure TiO_2 and ZnO are indeed used as physical sunscreens, I find it extremely hard to believe that they make any difference at the levels of concentration found in the Isinuka clays, especially because both titanium and zinc in the analysed samples probably do not occur in the pure oxide forms, but rather as trace elements scattered throughout the crystal lattices of the minerals present in the samples.

I found the research question posed by the author extremely interesting and relevant to the South African context, as it relates to indigenous knowledge systems and issues of public health. However, I am troubled by this work given the inconsistencies highlighted above, especially because of the importance of this work for the continued wellbeing of the residents making use of the clays from the Isinuka springs, and because of the author's suggestion of certain, in my opinion unfounded, beneficial (UV protection as a result of the presence of Ti and Zn; absence of hexavalent Cr) and harmful (the possible presence of radioactive Sr) effects of exposure to the clay. It is my honest opinion that this work should not have been published in the *Transactions of the Royal Society of South Africa*, not because of a lack of originality or cross-disciplinary interest but because of what I deem to be a serious lack of even the most basic scientific rigour.