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Comment on "Phase analysis of iron oxides forming the red pigment layer of the ancient earthenwares excavated from the southern Korean Peninsula"

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In a wonderful attempt, Lee et al. [1] characterised eight ancient pottery samples procured during the excavation from the southern Korean peninsula. They reported their finding on various phase analyses by using several complementary techniques such as XRD, Raman and Mössbauer spectroscopy. I felt that the data collected is of rare and excellent quality, which they have subsequently attempted to analyse and interpret. Unfortunately, I would like to bring your kind attention to several errors in their analysis of Mössbauer spectroscopic data, carried out without considering the outcome of the complementary XRD and Raman spectroscopic studies. It resulted in missing mineral phase maghemite, its relative abundance in studied samples and subsequently affecting a significant portion of the discussion.

While we agree with the authors that it is always challenging to distinguish between hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) from Mössbauer spectra, most importantly, where they are associated with magnetite (Fe_3O_4), however, it is possible to distinguish them with the help of various complementary techniques such as XRD and Raman spectroscopy, similar to the present case [2, 3]. It is evident from Fig. 4 (XRD spectra) that while both magnetite (corresponds to the solid grey line) and maghemite (corresponds to the solid blue line) are present in lower concentration, none of the phases is absent in any sample, and even in some cases, the observed peak is prominent for the latter than the former. Interestingly in Raman spectra (in Fig. 5), maghemite can be identified with its broad characteristic bands in the region 341–350 cm^{-1}, 519–527 cm^{-1} along with bands in the 738–743 cm^{-1} range (strongest) [3]. Magnetite presence is evident from its characteristic band at the range of 671–674 cm^{-1}, also a strong maghemite band. The hematite presence is eminent from the characteristics XRD peaks (Fig. 4) and Raman band in the range of 223–229 cm^{-1} (strongest) with other bands in 244–252 cm^{-1}, 290–293 cm^{-1} and 406–411 cm^{-1} range. Hence, from XRD and Raman spectroscopy, the presence of hematite, maghemite and magnetite is confirmed in all these eight samples [4–6].

Accordingly, a fitting model should consist of two sextets corresponding to the hematite and maghemite phases, another two sextets representing tetrahedral and octahedral phases of magnetite along with a doublet attributed to ferrihydrite (total of 26 lines) as observed from Mössbauer spectra and missing from XRD due to their amorphous nature, would suffice to estimate the respective proportions of individual phases [7–10]. However, the authors' Mössbauer analysis ruled out the presence of maghemite, resulting in unreliable and unrelated observations. It is evident from Table 2, the contribution of hematite and magnetite is almost the same (the ratio is 1.15 ± 0.25; recalculated for eight samples from Table 2), which is contrary to the obtained information from complementary techniques XRD and Raman study. The missing sextet due to maghemite has significantly affected the analysed Mössbauer parameters.

For stoichiometric magnetite, the hyperfine parameters are well-established. At room temperature, isomer shift (relative to α-Fe) at 0.26 and 0.67 mm s^{-1}, quadrupole shift at 0.02 and 0.00 mm s^{-1} with expected hyperfine fields are 490 and 460kOe for tetrahedral and octahedral sites, respectively [9]. For these samples, the authors observed a higher hyperfine field for the tetrahedral site (502.6 ± 2.9kOe; recalculated from Table 2) after the fitting, which is the literature reported value for maghemite [10]. Similarly, the isomer shift obtained for the magnetite octahedral site

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(0.45 ± 0.03 mm s^{-1}; recalculated for eight samples from Table 2) is at the lower side but in the range for the reported values of maghemite [8–10]. In this context, it is necessary to include the estimated uncertainties and the line-width of individual sub-spectra in their Mössbauer spectral analysis. It is essential to report the goodness of fit to understand the quality fit and the procedure for obtaining hyperfine parameters. Furthermore, we would like to mention that the Fe–O asymmetric bending band in the 520–240 cm^{-1} range and the broad-band near 1310 cm^{-1} is not detected as described by the authors [1].

In summary, the authors missed the maghemite phase while analysing Mössbauer spectra presented in Fig. 6, resulting in an erroneous dataset in Table 2 and its subsequent interpretation. Their presentation of Mössbauer spectrum analysis lacks the estimated uncertainties of the measurement, and also, they have failed to quantify (or to present) the line-width of individual sub-spectra. The authors must provide a modified result after considering the mineral phases present in the studied materials, which is essential, as reports on these materials are scanty.

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