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Comment on #Spin crossover in (Mg,Fe)O: A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data#

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Comment on "Spin crossover in (Mg,Fe)O: A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data"

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ABSTRACT

Electronic spin-pairing transition of iron in magnesiowüstite-(Mg,Fe)O has been recently studied with X-ray emission and Mössbauer spectroscopies under high pressures. While these studies reported a high-spin to low-spin transition of iron to occur at pressures above approximately 50 GPa, the width of the observed transition varies significantly. In particular, Kantor *et al*. [Phys. Rev. B **73**, 100101 (2006)] reported that the transition in $(Mg_{0.8},Fe_{0.2})O$ occurs over a pressure range of approximately 50 GPa in high-pressure Mössbauer measurements. To account for the discrepancy in the transition pressure, Kantor *et al*. reanalyzed the X-ray emission spectra by Lin *et al*. [Nature **436**, 377 (2005)] using a simple spectral decomposition method and claimed that X-ray emission measurements are also consistent with a spin crossover of iron at high pressures. Here we show that the proposed fitting method is inadequate to describe the X-ray emission spectrum of the low-spin FeS_2 and would give an erroneous satellite peak (K_β') intensity, leading to an artificial high-spin component and, consequently, to invalid conclusions regarding the width of the pressure-induced transition in magnesiowüstite. Furthermore, we compare Kantor's Mössbauer data with other recent high-pressure Mössbauer studies and show that the width of the transition can be simply explained by different experimental conditions (sample thickness, diameter, and hydrostaticity).

Pressure-induced electronic spin-pairing transitions of iron in magnesiowüstite-(Mg,Fe)O have been reported by X-ray emission spectroscopy[1-3], Mössbauer spectroscopy[3-5], X-ray diffraction[2,4], and theoretical calculations[6-8]. While these experimental studies all support that a high-spin to low-spin transition of iron occurs at pressures above approximately 50 GPa [1-5], the reported width of the transition varies significantly from 18 GPa [2-4] to approximately 55 GPa [5]. On the other hand, recent theoretical predictions suggest that the transition in magnesiowüstite would occur over a very narrow range of pressure at room temperature but would turn into spin crossover with an extended pressure range of approximately 30 to 50 GPa at the lower mantle temperatures[7,8]. Since magnesiowüstite is considered to constitute a considerable volume fraction of the Earth's lower mantle (~20%), an understanding of the width of the transition is crucial to interpreting the consequent effects of the transition on the physical properties of magnesiowüstite in the Earth's lower mantle. Here we comment on the recent high-pressure Mössbauer study of $(Mg_{0.8},Fe_{0.2})O$ and the proposed alternative interpretation of the high-pressure X-ray emission spectra of $(Mg_{0.75},Fe_{0.25})O$ [5]. We show that the proposed spectral decomposition method is inadequate, leading to an erroneous interpretation of the transition pressure, and that the wide range of the transition pressures observed in [5] can be alternatively explained by the very thick, large sample and non-hydrostatic experimental conditions.

An electronic spin crossover of iron in $(Mg_{0.8},Fe_{0.2})O$ has been reported to occur from approximately 55 GPa to 105 GPa by high-pressure Mössbauer studies [5]. To account for the wide transition pressure and the discrepancy between Mössbauer and X-ray emission studies, a simple spectral decomposition method using a Pearson-IV peak shape and a Gaussian peak shape is used to reanalyze the X-ray emission spectra reported by

Lin *et al*. [2]. Using the same decomposition method, we show that the X-ray emission spectrum of the low-spin FeS_2, a commonly used standard in X-ray emission spectroscopy, can not be fitted with a simple Pearson-IV peak shape (Fig. 1(b)); a misfit occurs in the satellite peak region. Although the spectrum can be well fitted with two peaks, a Pearson-IV peak for the main $K_{\beta 1,3}$ peak and a Gaussian peak for the K_{β}' satellite peak as proposed by the authors [5], the use of the Gaussian peak produces an artificial high-spin component even though the sample is completely in the low-spin state (Fig. 1(a)). Consequently, the two-peak fitting method used for decomposing the X-ray emission spectra of the low-spin $(Mg_{0.75},Fe_{0.25})O$ would also give rise to an artificial, invalid satellite peak for the high-spin component with an average spin number of approximately one. That is, the fitting procedure with the Gaussian peak would always give a high-spin component and would not produce a single, complete low-spin component. As a matter of fact, independent analyses of the X-ray emission spectra of $(Mg_{0.75},Fe_{0.25})O$ [2] using crystal-field multiplet calculations by G. Vanko, F. de Groot[9], and J.P. Rueff[10] give results that are in agreement with what Lin *et al*. [2] had reported and consistent with recent synchrotron Mössbauer studies of the same compostion[3], as opposed to what is claimed by Kantor *et al*. [5].

To understand the electronic spin-pairing transition in the (Mg,Fe)O system, here we also report high-pressure X-ray emission spectra of $(Mg_{0.95},Fe_{0.05})O$ (Fig. 2). The very dilute concentration of Fe^{2+} in the sample allows observation of the transition at relatively low pressures[3]. The details of the XES experimental setup and interpretations of the XES spectra of the Fe-K_{β} lines are reported elsewhere[2,3]. All X-ray emission spectra of the sample were collected with the same system setup from the same sample, ensuring that the energy calibration remained intact through out the collection of the spectra. We

observed an energy decrease of ~1.6 eV in the $K_{\beta 1,3}$ main peak between 46 GPa and 55 GPa (Fig. 2b). The integrated and normalized intensity of the satellite peak of iron (K_{β}') in the sample as a function of pressure showed the presence of the satellite peak (K_{β}') below 46 GPa and the absence of the satellite peak above 55 GPa, indicating a high-spin to low-spin transition of iron between 46 GPa and 55 GPa. The energy shift of the main $K_{\beta 1,3}$ peak across the spin transition has been predicted by theory and has been explained by the preservation of the center of gravity of the spectra: when the high-spin satellite intensity disappears, main peak shifts towards the center of gravity of the emission spectrum in order to keep the center of the mass of the emission line fixed[11-13]. The observation of the energy shift is consistent with the change of the satellite intensity and can be used as an additional line of evidence for the electronic spin-pairing transition.

Furthermore, we have compared the abundance of the high-spin and low-spin states of iron in magnesiowüstite, as determined from recent high-pressure traditional[4,5] and synchrotron[3] Mössbauer spectroscopic measurements (Fig. 3). The range of the observed transition pressure varies significantly from 18 GPa at 300 K for $(Mg_{0.75},Fe_{0.25})O$ [3], to 20 GPa at 6 K for $(Mg_{0.8},Fe_{0.2})O$ [4], to approximately 50 GPa at 300 K for $(Mg_{0.8},Fe_{0.2})O$ [5]. The slight compositional variation in these experiments is unlikely to significantly affect the width of the transition and the transition pressure [3]. A narrower width of the transition was observed when a thin sample of 1 μm in thickness with an X-ray source of 7 μm in diameter and NaCl pressure medium was used, in agreement with the X-ray emission studies, whereas a thick, large sample of 25 μm in thickness and 125 μm in diameter without any pressure medium resulted in a transition pressure of 50 GPa [5], a much extended pressure range than other two studies[3,4]. That is, experimental

conditions significantly affect the width of the transition. The width of the transition pressure of ~18 GPa in $(Mg_{0.75},Fe_{0.25})O$ from Mössbauer spectroscopic measurements is also consistent with the X-ray emission measurements[2,3,9]. The thickness effects as well as non-hydrostatic conditions can also lead to difficulties in estimating the relative abundance of the high-spin and low-spin components using a linear modeling.

In conclusion, we presented X-ray emission and Mössbauer data of magnesiowustite to show that the X-ray emission analysis method proposed by Kantor *et al*. [5] is ill-founded and the extended width of the transition pressure in their Mössbauer measurements was due to very thick, large sample under non-hydrostatic conditions. Based on both high-pressure X-ray emission and Mössbauer results, we showed that the electronic spin-pairing transition of iron in $(Mg_{0.75},Fe_{0.25})O$ should be completed in less than 18 GPa.

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References

[1]. J. Badro, G. Fiquet, F. Guyot, J.P. Rueff, V.V. Struzhkin, G. Vankó, and G. Monaco, Science **300,** 789 (2003).

[2]. J.F. Lin, V.V. Struzhkin, S.D. Jacobsen, M. Hu, P. Chow, J. Kung, H. Liu, H.K. Mao, and R.J. Hemley, Nature **436**, 377 (2005).

[3]. J.F. Lin, A.G. Gavriliuk, V.V. Struzhkin, S.D. Jacobsen, W. Sturhahn, M.Y. Hu, P. Chow, and C.S. Yoo, Phys. Rev. B **73**, 113107 (2006).

[4]. S. Speziale, A. Milner, V.E. Lee, S.M. Clark, M. Pasternak, and R. Jeanloz, Proc. Natl. Acad. Sci. **102**, 17918 (2005).

[5]. I.Yu. Kantor, L.S. Dubrovinsky, and C.A. McCammon, Phys. Rev. B **73**, 100101 (2006).

[6]. D.M. Sherman, J. Geophys. Res. **96**, B9, 14299 (1991).

[7]. W. Sturhahn, J.M. Jackson, and J.F. Lin, Geophys. Res. Lett. **32**, L12307 (2005).

[8]. T. Tsuchiya, R.M. Wentzcovitch, C.R.S. da Silva, and S. de Gironcoli, Phys. Rev. Lett. **96**, 198501 (2006).

[9]. G. Vankó and F. de Groot, submitted to Phys. Rev. B (2006).

[10]. J.P. Rueff (Private Communication).

[11]. F. de Groot, Chem. Rev. **101,** 1779 (2001).

[12]. P. Glatzel and U. Bergmann, J. Am. Chem. Soc.**126**, 9946 (2004).

[13]. P. Glatzel and U. Bergmann, Coord. Chem. Rev. **249**, 65 (2005).

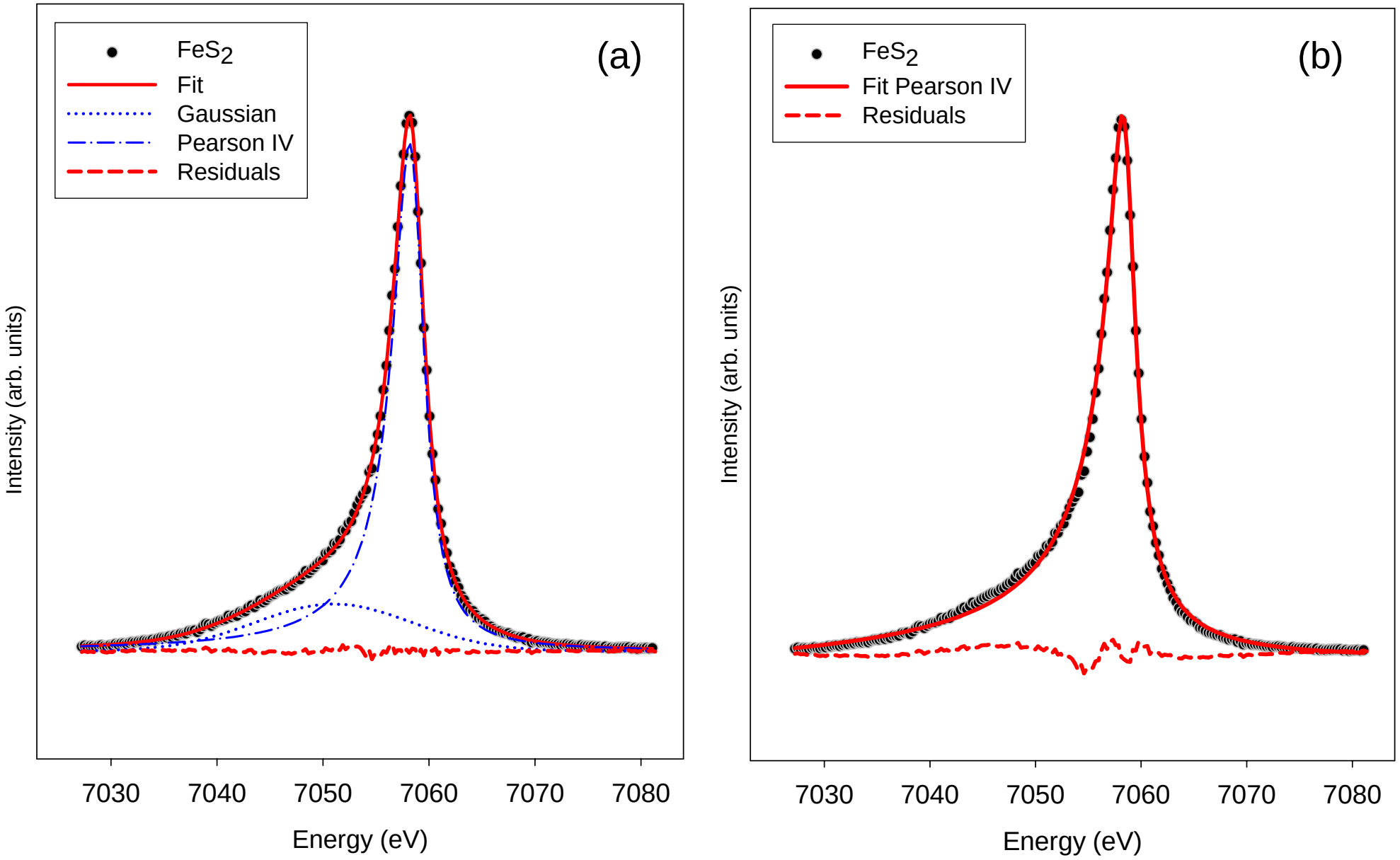
Figure Captions:

FIG. 1. X-ray emission spectrum of the low-spin FeS_2 at ambient conditions (black dots). (a) Red line, fitting with Kantor's decomposition model[5]; Blue dashed-dotted line: fitting with a Pearson-IV peak; blue dotted line: fitting with a Gaussian peak; red dashed line: residuals. (b) Red line, fitting with a Pearson-IV peak; red dashed line: residuals. We note that FeS_2 is known to be in low-spin state under ambient conditions. The fitting based on Kantor's model gives an erroneous satellite peak (Figure 1(a), blue dotted line), whereas a misfit occurs in the satellite peak region when fitting with a single Pearson-IV peak (Figure 1(b)).

FIG. 2. Representative X-ray emission spectra of Fe-K_β collected from magnesiowüstite [$(Mg_{0.95},Fe_{0.05})O$] at high pressures. The spectrum at ambient conditions was measured outside the diamond anvil cell. The original spectra without normalization and energy shifting are plotted in the main panel. (a) Integrated and normalized intensity of the satellite peak as a function of pressure. The intensity of the satellite peak was obtained by subtracting each spectrum from the one at the highest pressure (low-spin state) [2]. The errors in integrated intensity were propagated from statistical errors in original spectra. (b) Energy shift of the main emission peak ($K_{\beta 1,3}$) as a function of pressure. We note that the energy the $K_{\beta 1,3}$ of iron in $(Mg_{0.95},Fe_{0.05})O$ was located at ~7058 eV, and an energy decrease of ~1.6 eV was observed between 46 GPa and 55 GPa.

FIG. 3. Abundance of high-spin and low-spin states of iron in magnesiowüstite, as determined from recent high-pressure Mössbauer spectroscopic measurements[3-5]. Open circles, $(Mg_{0.75},Fe_{0.25})O$ at high pressures and 300 K [3]; open triangles, $(Mg_{0.80},Fe_{0.20})O$

at high pressures and 6 K [4]; dashed line, $(Mg_{0.80},Fe_{0.20})O$ at high pressures and 300 K [5].


FeS2
Fit
Gaussian
Pearson IV
Residuals
(a)
Intensity (arb. units)
7030
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7050
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Energy (eV)
FeS2
Fit Pearson IV
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(b)
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7030
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Energy (eV)

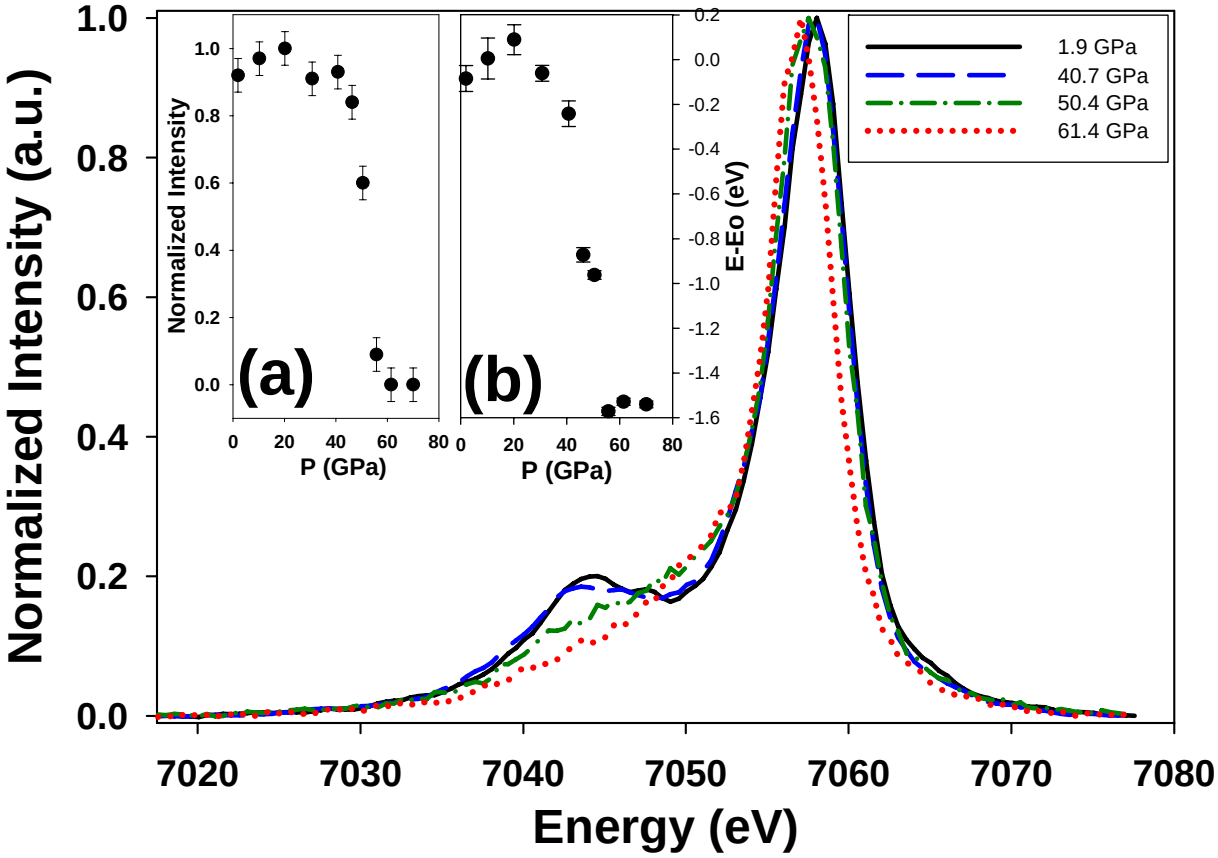
Normalized Intensity (a.u.)
Energy (eV)
1.9 GPa
40.7 GPa
50.4 GPa
61.4 GPa
(a)
(b)
Normalized Intensity
E-Eo (eV)
P (GPa)
P (GPa)

FIG. 2

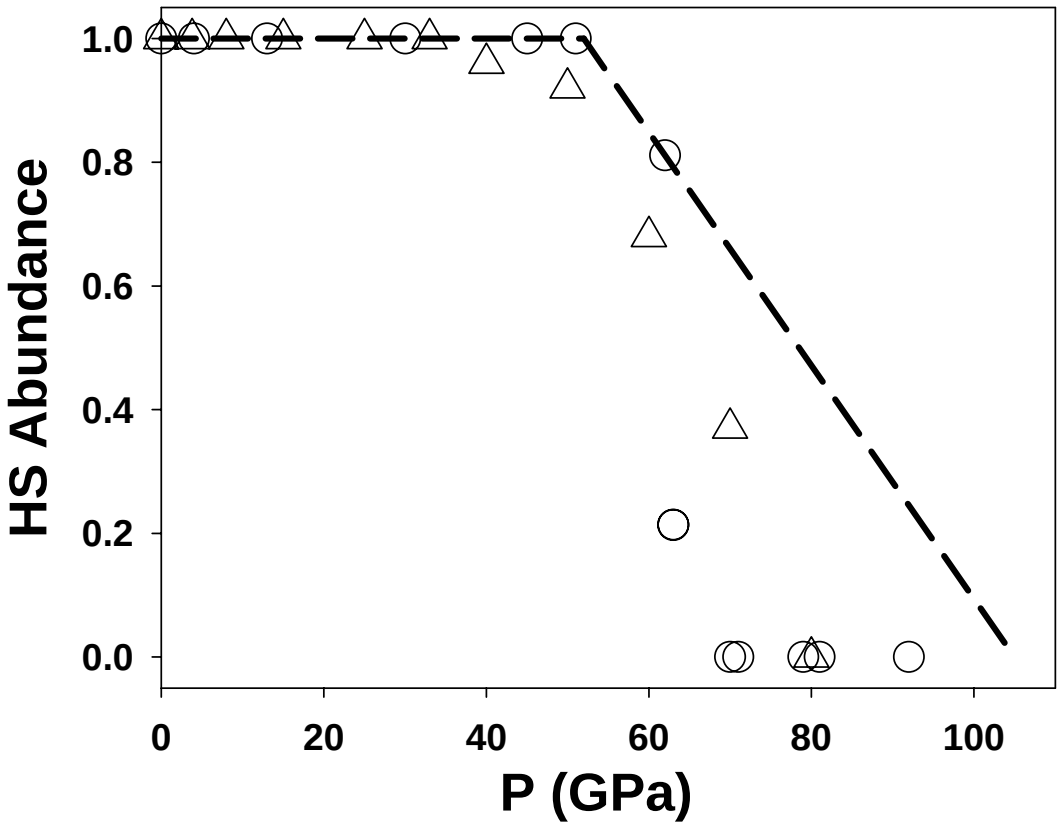

FIG. 3