ASP Dissolved Inorganic Carbon and Stable Isotope Intercalibration Report

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1 Participation on DIC analyses
2 Participation on stable isotopes analyses

Introduction and Field

The Arctic Science Partnership (ASP) is a network of universities and institutes that aims to study and monitor the Artic environment. Due the size of ASP network, it has a framework of thematic teams with representatives from each member institution. The *Lab Team* is part of this framework, and it exists to verify the quality of analyses done within the network and improve them wherever possible.

Here we outline an assessment of the Dissolved Inorganic Carbon (DIC) and Stable Isotope (δ^{18}O and δ^{2}H) within the ASP Lab Team, routine parameters that are used to many studies.

DIC assessment had water samples with low salinity for this intercomparison and were collected from a hydroelectric generating station on the Nelson River, in Gillam, Manitoba. High salinity samples were collected in the Pacific Ocean provided by Scripps Institution of Oceanography of the University of California, San Diego.

Stable Isotope assessment had ice core samples were collected from McGill Arctic Research Station (MARS) is located at the head of Expedition Fjord on west side of Axel Heiberg Island, collected by Dorthe Dahl-Jensen team.

Methods

Low salinity water samples were collected from water intakes of the Keeyask hydroelectric generating station on the Nelson River that is approximately 30 km upstream from Gillam Manitoba, approximately 10m depth. The water samples were refrigerated and send right way to UM and then preserved with saturated mercury chloride. High salinity water samples were collected in Pacific Ocean by University of California. The sea water was sterilized by a combination of filtration, ultra-violet radiation and addition of mercuric chloride (Dickson, 2022). Both water types were sent to three different labs, Aarhus University (AU), University of Manitoba (UM), and Greenland Institute of Natural Resources (GINR) for DIC analyses.

For DIC analyses of seawater and freshwater samples were transferred to gas-tight vials (12mL Exetainer, Labco High Wycombe, UK), poisoned with 12 µL solution of saturated $HgCl_2$, and stored in the dark at room temperature until analysis. DIC was measured on a DIC analyzer (Apollo SciTech) by acidification of a 0.75 mL or 0.9 mL subsample with 1 mL 10% H_3PO_4 and quantification of the released CO_2 with a nondispersive infrared CO_2 analyzer (LI-COR, LI-7000, Lincoln, NE, USA). Results were then converted from µmol L^{-1} to µmol kg^{-1} based on sample density, which was estimated from salinity and temperature. An accuracy of 6 µmol kg^{-1} or lower was determined for DIC from routine analysis of certified reference material (A.G. Dickson, Scripps Institution of Oceanography, San Diego, CA, USA).

Ice core samples were collected at MARS station, subsequently they were subsampled with 2cm sections and sent to four laboratories, Aarhus University (AU), University of Manitoba (UM), and University of Alberta (UA), and University of Copenhagen (UC) for stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) analysis.

The laboratory participants used Cavity Ringdown Spectrometer (Picarro Inc., USA) for stable isotope, the calibration range were from $\delta^{18}O$ (-2.2 to -55.5) and $\delta^{2}H$ (-2.0 to -427.5). Dissolved Inorganic Carbon Analyzer from Apollo SciTech, USA, were used for DIC analyses and the calibration range were from 200 to 2500 µmol L^{-1}, Table 1.

The stable isotopes were analyzed using a Cavity Ringdown Spectrometer, L2130-*i* or L3240-*i* models couple with A0211, a vaporization module (Picarro Inc., USA). Several replicates are taken from each sample and first ones are excluded in order to remove any residual carryover from the previous sample. Depending of the laboratory, from one up to three certified reference materials were used, as well internal lab standard. The external standards used to calibrate the results were Vienna Standard Ocean Water 2 (VSMOW2), Greenland Ice Sheet Precipitation (GISP), GRESP (Greenland Summit Precipitation) and Standard Light Antarctic Precipitation 2 (SLAP2), Table 1.

Table 1: Instrument and calibration information used for DIC and stable isotopes comparison exercise of ASP laboratories

	Stable Isotopes		DIC	
Laboratory	Instrument (make/model)	Calibration standards	Instrument (make/model)	Calibration standards (µmol/L)
Manitoba	L2130-*i*	$\delta^{18}O$ (0; -24.8; -55.5) $\delta^{2}H$ (0; -189.5; -427.5)	Apollo SciTech (AS-3)	200 to 2000
Aarhus	L2130-*i*	$\delta^{18}O$ (0; -33.4; -55.5) $\delta^{2}H$ (0; -258.0; -427.5)	Apollo SciTech (AS-C5)	1200 to 2500
Alberta	L2140-*i*	$\delta^{18}O$ (-2.2 and-55.5) $\delta^{2}H$ (-2.0 and -394.7)	N.D.	N.D.
Copenhagen	L2140-*i*	$\delta^{18}O$ (0.03) $\delta^{2}H$ (0.39)	N.D.	N.D.
GINR	N.D.	N.D.	Apollo SciTech (AS-3)	1050 to 2100

N.D.: No data

Data Discussion

Stable Isotopes

Samples collected from MARS were sent to participants laboratories for Stable Isotope ($\delta^{18}O$ and $\delta^{2}H$) analyses. Each lab has their own procedure to analyze samples. Their different protocols (Table 2) and data are discussed below and summarized in Table 3.

Table 2: Stable isotopes analyses protocols from the ASP laboratories

	Stable Isotopes			
	UM	AU	UA	UC
Inj per vial (sample)	9	6	12	4
Inj discard (sample)	6	1	8	1
External std (#)	3	3	2	1
Cal between batch	6	15	1	1
Internal std intervals	6	15	10	3-50

AU: Aarhus University; UA: University of Alberta; UC: University of Copenhagen; UM: University of Manitoba;

UM analyzed full ice core and the average standard deviation was for $\delta^{18}O$ 0.08‰ and $\delta^{2}H$ 0.42‰ for 790 ice core slices. UM had most ice core slices among the participant labs, other labs participated partially, sole for the intuit of this lab intercomparison.

UA analysis had average standard deviation of $\delta^{18}O$ 0.04‰ and $\delta^{2}H$ 0.10‰ for 163 ice core slices, the second largest samples analyzed for comparison.

AU analysis had average standard deviation of $\delta^{18}O$ 0.04‰ and $\delta^{2}H$ 0.21‰ for 40 ice core slices.

Unfortunately, we do not have UC analysis average standard deviation for 40 ice core slices.

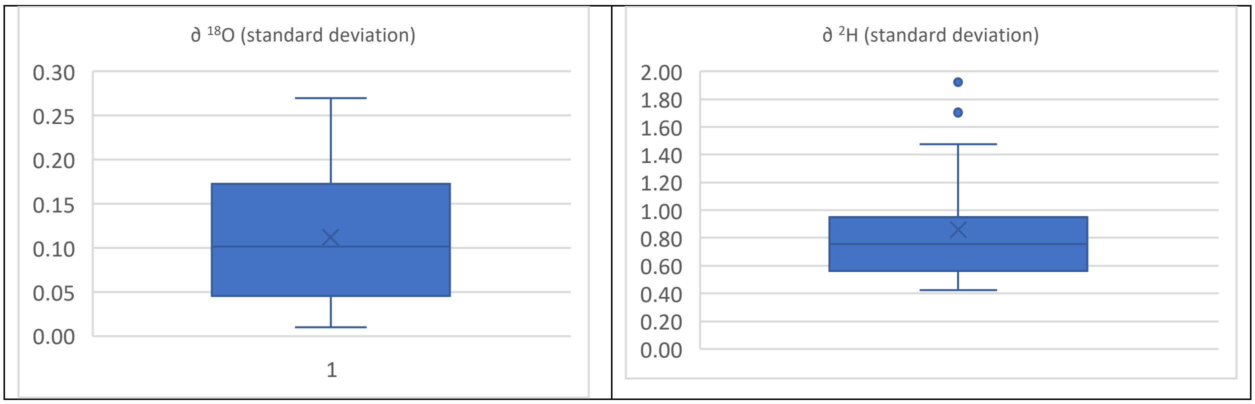
Table 3: Stable isotopes standard deviation from the ASP laboratories

Stable Isotopes				
	UM	AU	UA	UC
$\delta^{18}O$ (S.D.)	0.08	0.04	0.04	N.D.
$\delta^{2}H$ (S.D.)	0.42	0.21	0.10	N.D.

AU: Aarhus University; UA: University of Alberta; UC: University of Copenhagen; UM: University of Manitoba.
N.D.: No data, S.D.: Standard Deviation

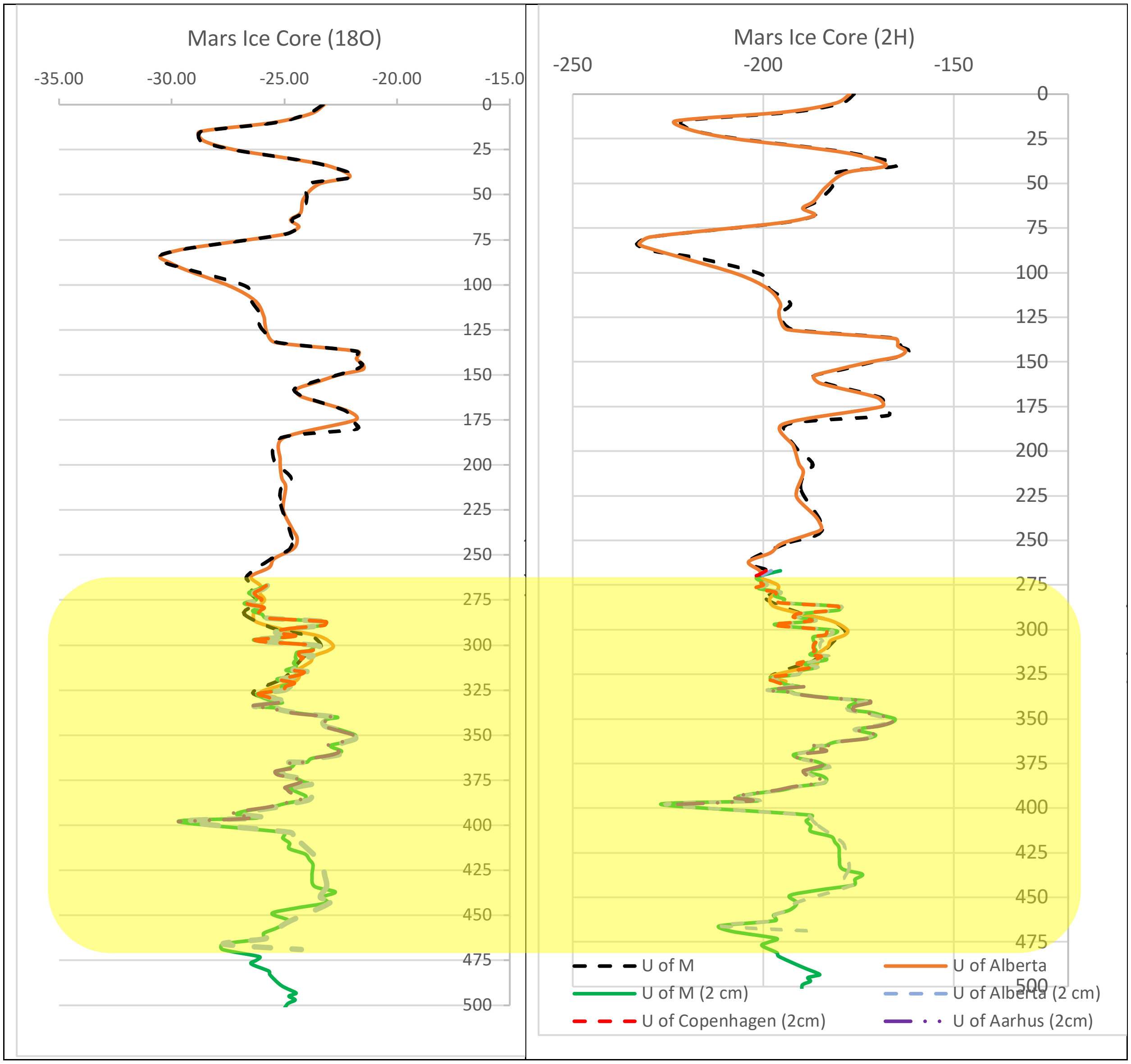
Even each laboratory has different protocols for calibration, for instance, UM calibrates with 3 external standards for each 6 samples, AU also with 3 external standards calibrates each 15 samples, UA and UC have 1 external standard for whole batch. The intercalibration data shows all four labs had standard deviation distribution of $\delta^{18}O$ 0.11‰ and $\delta^{2}H$ 0.85‰. The $\delta^{18}O$ 0.11‰ and $\delta^{2}H$ 0.85‰ are in good agreement according to a worldwide proficient test by International Atomic Energy Agency (Wassenaar et al., 2012), Graph1.

The outliners on $\delta^{2}H$ of Graph 1 appears to be random analytical issues, because is not come from a specific laboratory.



Graph 1: Standard deviation from stable isotope data of $\delta^{18}O$ and $\delta^{2}H$ from the four ASP labs

UM analyzed full ice core, 790 ice slices, and three labs participated on a partial core analysis as interlaboratory comparison. The participation of the laboratories was in the middle section of the ice core, between 275 and 400. A partial stable isotopes profile from MARS ice ore is showing in the Graph 2. The highlighted area shows the excellent agreement among the participant labs in this exercise, despite with the labs having different protocols for calibration and frequency of calibration.



Graph 2: Ice core profile showing $\delta^{18}O$ and $\delta^{2}H$

Dissolved Inorganic Carbon

Low and high salinity samples were sent to participant laboratories for Dissolved Inorganic Carbon analyses. All laboratories used Apollo SciTech analyzer, AU has an upgrade model than UM and GINR, Table 1.

UM analyzed both type of water, given 1804.8 µmol/Kg for low salinity sample and 2039.3 µmol/Kg for high salinity samples. UM analyzes standards after each 6 samples due to drift correction. UM used calibration range from 200 to 2000 µmol/Kg and the ionic strength of titrant was adjusted to 0.7M for high salinity and no ionic strength was adjusted of titrant for low salinity samples, Table 4.

AU analyzed both type of water, given 1737.4 µmol/Kg for low salinity sample and 2022.2 µmol/Kg for high salinity samples. AU analyzes standards after each 3 samples due to drift correction. AU used calibration range from 1200 to 2500 µmol/Kg and no adjustment on ionic strength for high salinity was done for these analyses, Table 4.

GINR analyzed both type of water, given 1775.6 µmol/Kg for low salinity sample and 2035.2 µmol/Kg for high salinity samples. GINR analyzes standards after each 6 samples due to drift correction. GINR used calibration range from 1050 to 2100 µmol/Kg and no adjustment on ionic strength for high salinity was done for these analyses, Table 4.

Table 4: DIC analyses from the ASP laboratories.

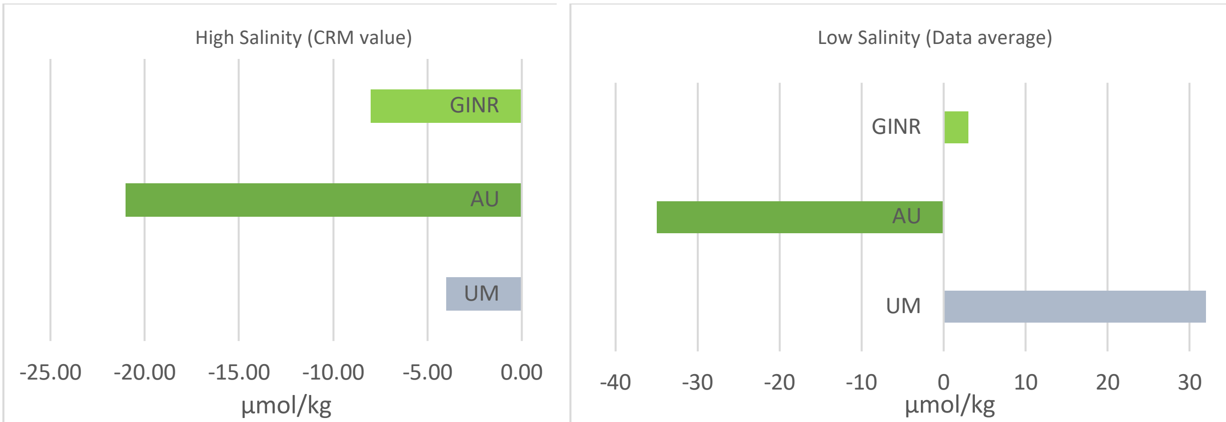
	Dissolved Inorganic Carbon			
	Salinity	UM µmol/Kg	AU µmol/Kg	GINR µmol/Kg
Low Salinity (Mean)	0.17	1804.4 ± 4.7	1737.4 ± 5.1	1775.6 ± 7.6
High Salinity (Mean)	33.35	2039.3 ± 0.6	2022.2 ± 1.6	2035.8 ± 1.9

UM: University of Manitoba; AU: Aarhus University; and GINR: Greenland Institute of Natural Resources

In this exercise the high salinity samples came from seawater with DIC certified values of 2043 ± 0.62 µmol/. AU had difference of 21 µmol/Kg from the certified value, GINR had 8 µmol/Kg, and UM had 4 µmol/Kg (Table 2 and Graph 3). There isn't an apparent explanation why AU had bigger difference than other labs. All labs had samples within the calibration curve range and had drift corrected on the analysed batch.

Low salinity samples came from a river, northern Manitoba, the reference value used for comparison was the total average of samples (1772 µmol/Kg). GINR had 3 µmol/Kg difference from total average and UM and AU had 32 µmol/Kg and 35 µmol/Kg, respectively (Table 2 and Graph 3).

The number of labs that participated in this exercise are too small to draw a conclusion but it seems low salinity samples need further study. Two of three labs gave around 30 µmol/Kg that is considered a big difference to have for oceanographic study.



Graph 3: Difference in µmol/kg values from certified values (high salinity) and sample's average (low salinity).

Conclusions and Recommendations

Stable Isotopes

The data presented in this report suggests that the stable isotope analyzed using Cavity Ringdown Spectrometer (Picarro Inc., USA) is very precise instrument to analyse ice cores. The intercalibration data shows all four labs had average standard deviation distribution of $\delta^{18}O$ 0.11‰ and $\delta^{2}H$ 0.85‰. The $\delta^{18}O$ 0.11‰ and $\delta^{2}H$ 0.85‰ are in good agreement according to a worldwide proficient test by International Atomic Energy Agency (Wassenaar et al., 2012).

Beside each laboratory has different protocols for calibration but there are no apparent consequences on the precision of the analyses.

Dissolved Inorganic Carbon

The small number of laboratories participants in this exercise affected a good evaluation. In this exercise the high salinity has a DIC certified values of 2043 ± 0.62 µmol/kg that helps to evaluate the precision of each laboratory, even with a small number of participants. Two of three labs have standard deviation less than 10 µmol/kg, showing a fair precision. All labs had samples within the curve range and had drift corrected on the analysed batch.

Although, for low salinity samples, the small number of laboratories impacted the evaluation due to, a) not having a sample with a certified values or recommended value and b) small number of lab participation. Two of labs had about 30 µmol/kg difference from total average, that would be considered the "true" value. A large number of laboratories participating would give more precise "true" value of the sample, consequently better evaluation of DIC in low salinity samples.

Acknowledgments

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References

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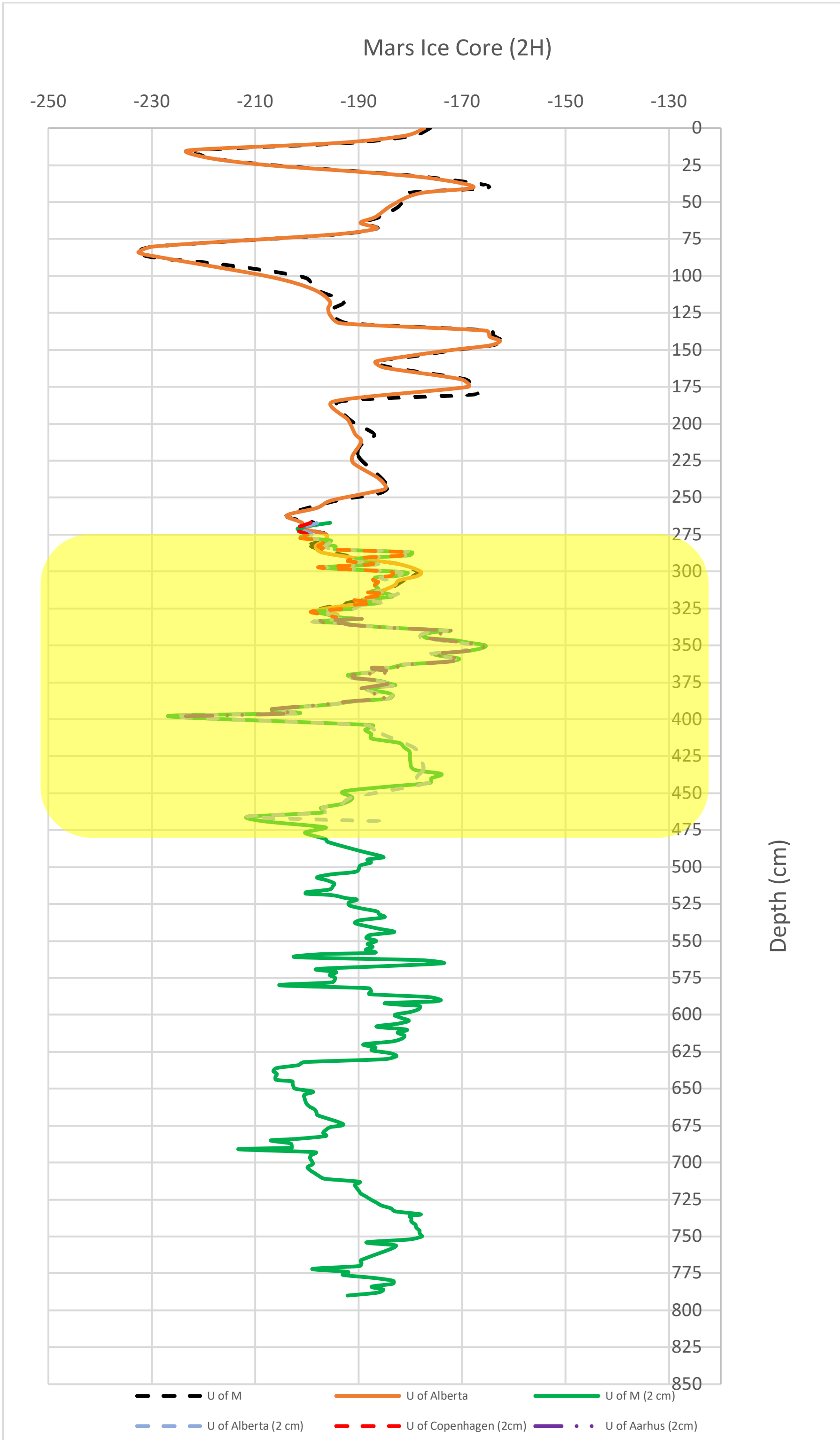
Appendix



Full ice core profile showing $\delta^{18}O$ and $\delta^{2}H$