IAEA

2nd INTERLABORATORY COMPARISON FOR DEUTERIUM AND OXYGEN-18 ANALYSIS OF WATER SAMPLES

REPORT

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1. INTRODUCTION

The IAEA Isotope Hydrology Laboratory organised in 1998/99 the 2nd interlaboratory comparison test for analytical laboratories engaged in routine analyses of hydrogen and oxygen stable isotope composition of water samples. This intercomparison exercise was carried out in the framework of the Analytical Quality Control Services (AQCS) programme of the International Atomic Energy Agency. The first interlaboratory comparison test of this kind carried out in 1995 was restricted to laboratories analysing, on a regular basis, precipitation samples collected in the framework of the Global Network "Isotopes in Precipitation" (GNIP), jointly operated by IAEA and WMO (Araguás-Araguás and Rozanski, 1995). The current test was open to all laboratories engaged in isotope analyses of water samples.

The interlaboratory comparison was announced in December 1998 on the Internet, via the ISOGEOCHEM news group. Moreover, invitation letters were send out to all GNIP laboratories. Although the main objective of this exercise was to help the laboratories engaged in stable isotope analyses of water samples to assess their precision and accuracy for the range of $\delta^{18}O$ and $\delta^{2}H$ values normally observed in meteoric waters, it was decided that after completion of the exercise the analysed batches of water will be stored at the IAEA Isotope Hydrology Laboratory. They will serve as calibrated samples with the purpose to check the calibration of internal standards, and will be available on cost-free basis. It was therefore important to calibrate these materials with the smallest attainable uncertainty. To reach this goal, the IAEA specially invited seven laboratories known for the high quality of their analytical work to join the exercise and to provide the consensus values of the analysed waters. Four laboratories belonging to this group recently participated in the calibration of a successor material for VSMOW (M. Gröning – report in preparation).

More than one hundred laboratories from 43 countries indicated their willingness to participate in the exercise and received four water samples for analysis (IC-OH-1 to IC-OH-4, in the following indicated as OH-1 to OH-4). By the end of April 1999, 87 laboratories had returned the results to the IAEA (see list of participants in Annex 1.) Two laboratories - ID no. 112 and 134- reported only after the deadline: their results are listed, but have not been used for the evaluation. Each laboratory received a reporting sheet (see Annex II), requesting details of their sample preparation techniques and normalisation procedures. The laboratories were requested to report the δ-values on the normalised VSMOW-SLAP scale, together with the overall uncertainty (one-sigma level).

The four water samples distributed among the participating laboratories cover the range of $\delta^{18}O$ and $\delta^{2}H$ values typical for the majority of natural waters. The samples were bottled from 60 l stainless steel storage barrels into 50 ml double capped brown glass bottles, serially numbered. Each laboratory received four samples with corresponding label numbers. These label numbers were further used throughout the exercise as laboratory identification (ID) numbers and are also used in the tables and graphs within this report. The ID numbers are not related to the list of participating laboratories given in Annex II.

2. PRESENTATION OF THE RESULTS

Tables 1 and 2 summarise the results of oxygen-18 and deuterium analyses of the intercomparison samples, as submitted by the laboratories participating in the exercise. The laboratories are identified by the assigned ID numbers (first column). The stated uncertainties are those quoted by the individual laboratories as one-sigma standard uncertainties. Although the laboratories have been asked to provide uncertainties assessed by a complete uncertainty budget or by the long-term standard deviation of internal laboratory standards (instructions given in the reporting sheet), most laboratories evaluated the uncertainty of the results only by using the standard deviation of individual measurements of the provided four samples. This has to be kept in mind for any quantitative assessment of the laboratory performance. All values are expressed in delta notation, normalised to the VSMOW-SLAP scale (Coplen et al., 1996).

Lab. ID no.	Preparation method	IC-OH-1 dO-18 vs. VSMOW [‰]	±1 sigma	IC-OH-2 dO-18 vs. VSMOW [‰]	±1 sigma	IC-OH-3 dO-18 vs. VSMOW [‰]	±1 sigma	IC-OH-4 dO-18 vs. VSMOW [‰]	±1 sigma
10	CO2-eq	-0.04	0.05	-3.27	0.06	-8.60	0.04	-15.27	0.05
12	CO2-eq	0.20	0.40	-3.10	0.40	-8.60	0.40	-15.20	0.40
13	CO2-eq	-0.04	0.02	-3.28	0.02	-8.64	0.02	-15.27	0.02
14	CO2-eq	-0.20	0.50	-4.10 #	0.50	-9.00	0.50	-15.70	0.50
15	CO2-eq	-0.13	0.06	-3.33	0.05	-8.69	0.05	-15.30	0.05
16	CO2-eq	-0.22 x	0.06	-3.38	0.06	-8.74	0.06	-15.32	0.06
17	CO2-eq	-0.09	0.10	-3.37	0.10	-8.77	0.15	-15.49	0.20
19	CO2-eq	-0.02	0.10	-3.25	0.10	-8.67	0.10	-15.33	0.10
21	CO2-eq	-0.90 #	0.20	-3.40	0.20	-8.60	0.20	-15.00	0.20
22	CO2-eq	0.06 x	0.04	-3.27	0.05	-8.86 x	0.03	-15.76 x	0.04
24	CO2-eq	-0.10	0.06	-3.33	0.06	-8.60	0.06	-15.32	0.06
25	CO2-eq	-0.35	0.20	-3.52	0.20	-8.85	0.20	-15.35	0.20
26	CO2-eq	-0.05	0.07	-3.18	0.07	-8.69	0.07	-15.23	0.07
27	CO2-eq	-0.15	0.10	-3.30	0.10	-8.69	0.10	-15.31	0.10
28	CO2-eq	-0.17	0.10	-3.42	0.10	-8.80	0.10	-15.32	0.10
29	CO2-eq	0.00	0.30	-3.60	0.30	-8.60	0.30	-15.50	0.30
31	CO2-eq	-0.05	0.05	-3.25	0.05	-8.66	0.05	-15.34	0.05
32	CO2-eq	-0.08	0.05	-3.32	0.05	-8.74	0.05	-15.31	0.05
33	CO2-eq	-0.30 x	0.10	-3.50 x	0.10	-8.90 x	0.10	-15.60 x	0.10
34a	CO2-eq	-0.02	0.06	-3.11 x	0.07	-8.52 x	0.06	-15.20	0.05
35	CO2-eq	0.04	0.06	-3.17 x	0.05	-8.53 x	0.04	-15.11	0.12
36	CO2-eq	-0.09	0.04	-3.16 x	0.04	-8.61	0.05	-15.20	0.06
39	CO2-eq	-0.07	0.06	-3.39	0.07	-8.88 x	0.06	-15.67 x	0.10
42	CO2-eq	-0.24	0.10	-3.43	0.10	-8.86	0.15	-15.49	0.15
43	CO2-eq	-0.01	0.06	-3.16 x	0.04	-8.47	0.11	-15.26	0.07
44	CO2-eq	-0.07	0.09	-3.19	0.12	-8.58	0.14	-15.25	0.14
45	CO2-eq	0.51 #	0.33	-2.71 x	0.26	-7.80 #	0.15	-14.50 #	0.19
46	CO2-eq	-0.09	0.09	-3.30	0.09	-8.68	0.09	-15.36	0.09
47	CO2-eq	-0.20	0.10	-3.50 x	0.10	-8.80	0.10	-15.30	0.10
51	CO2-eq	0.00	0.22	-3.98 x	0.22	-8.92	0.22	-15.50	0.22
52	CO2-eq	-0.15 x	0.05	-3.30	0.05	-8.85 x	0.05	-15.45 x	0.05
53	CO2-eq	-0.08	0.04	-3.29	0.02	-8.67 x	0.01	-15.32 x	0.01
54	CO2-eq	-0.05	0.05	-3.22	0.05	-8.61	0.05	-15.29	0.05
55	CO2-eq	-0.01	0.06	-3.26	0.06	-8.61	0.06	-15.28	0.06
58	CO2-eq	-0.07	0.04	-3.27	0.04	-8.67	0.05	-15.30	0.06
61	CO2-eq	-0.14	0.08	-3.36	0.08	-8.67	0.08	-15.22	0.08
62	CO2-eq	-0.07	0.14	-3.36	0.08	-8.67	0.08	-15.34	0.08
64	CO2-eq	-0.22	0.10	-3.43 x	0.07	-8.77	0.07	-15.39	0.09
65	CO2-eq	-0.01	0.08	-3.20	0.08	-8.57	0.08	-15.16	0.08
67a	CO2-eq	-0.02	0.05	-3.25	0.05	-8.67	0.05	-15.32	0.03
68	CO2-eq	0.02	0.08	-3.21	0.08	-8.61	0.08	-15.27	0.08
69	CO2-eq	-0.26 x	0.07	-3.49 x	0.06	-8.95 x	0.06	-15.66 x	0.05

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Table 1, part 1/2: The results of $\delta^{18}O$ analyses of four intercomparison samples (OH-1, OH-2, OH-3, OH-4) and the associated standard uncertainty, as reported by the laboratories participating in the interlaboratory comparison. Symbols (#) and (x) mark the results rejected in the first and second step of the statistical treatment, respectively; see also part 2 on next page.

Lab. ID no.	Preparation method	IC-OH-1 dO-18		IC-OH-1 ±1 sigma vs. VSMOW [‰]	IC-OH-2 dO-18		IC-OH-2 ±1 sigma vs. VSMOW [‰]	IC-OH-3 dO-18		IC-OH-3 ±1 sigma vs. VSMOW [‰]	IC-OH-4 dO-18		IC-OH-4 ± sigma vs. VSMOW [‰]
		continuation of the table from previous page											
71	CO2-eq	-0.13		0.14	-3.15		0.14	-8.49		0.13	-15.17		0.09
72	CO2-eq	0.01		0.15	-3.25		0.15	-8.53		0.15	-15.29		0.15
73	Hydrochloride	-0.20		0.20	-2.80		0.70	-8.00	#	0.50	-14.90		0.20
75	CO2-eq	-0.23	x	0.08	-3.34		0.08	-8.68		0.08	-15.36		0.08
78	CO2-eq	-0.08		0.05	-3.32		0.05	-8.72		0.05	-15.38		0.05
79	CO2-eq	-0.16	x	0.03	-3.43	x	0.04	-8.74		0.05	-15.44	x	0.05
82	CO2-eq	-0.08		0.10	-3.30		0.10	-8.68		0.10	-15.31		0.10
83	CO2-eq	-0.23	x	0.04	-3.47	x	0.08	-8.87	x	0.07	-15.43	x	0.05
85	CO2-eq	0.59	#	0.02	-2.65	x	0.04	-8.22	x	0.02	-15.05	x	0.03
86	CO2-eq	0.14	x	0.04	-3.11	x	0.04	-8.51	x	0.04	-15.21		0.04
88	CO2-eq	-0.18		0.12	-3.35		0.17	-8.61		0.17	-15.30		0.14
89	-	-		-	-		-	-		-	-		-
93	CO2-eq	-0.31	x	0.09	-3.47	x	0.08	-8.89	x	0.05	-15.54	x	0.03
94	-	-		-	-		-	-		-	-		-
96	CO2-eq	-0.11		0.10	-3.33		0.10	-8.71		0.10	-15.35		0.10
97	CO2-eq	0.04		0.05	-3.17	x	0.05	-8.57		0.07	-15.23		0.07
99	CO2-eq	-0.05		0.08	-3.29		0.08	-8.66		0.08	-15.27		0.08
101	CO2-eq	-0.06		0.11	-3.20		0.16	-8.31	x	0.11	-14.88	x	0.15
105	GC	-3.30	#	0.20	-6.60	#	0.20	-12.10	#	0.60	-18.00	#	0.10
106	CO2-eq	-0.81	#	0.25	-4.11	#	0.26	-9.32	#	0.15	-15.88	x	0.14
107	CO2-eq	-0.45		0.30	-3.72		0.30	-8.96		0.30	-15.54		0.30
108	CO2-eq	0.00		0.10	-3.27		0.10	-8.65		0.10	-15.32		0.10
109	CO2-eq	-0.14	x	0.02	-3.27		0.02	-8.77	x	0.04	-15.39	x	0.02
111	CO2-eq	-0.07		0.07	-3.31		0.07	-8.67		0.07	-15.32		0.07
113	CO2-eq	-0.16	x	0.05	-3.47	x	0.05	-8.66		0.11	-15.38		0.07
114	CO2-eq	-0.22		0.10	-3.45		0.10	-8.88	x	0.10	-15.48		0.10
115	CO2-eq	-0.01		0.04	-3.28		0.05	-8.63		0.02	-15.40	x	0.05
116	CO2-eq	-0.17	x	0.05	-3.36		0.07	-8.73		0.06	-15.35		0.06
117	CO2-eq	-0.17	x	0.05	-3.41	x	0.06	-8.73		0.07	-15.24		0.10
118	-	-		-	-		-	-		-	-		-
121	CO2-eq	-0.05		0.19	-3.25		0.19	-8.67		0.19	-15.33		0.19
122	CO2-eq	0.45	#	0.03	-2.87	x	0.03	-8.52	x	0.05	-15.37		0.08
123	CO2-eq	-0.17		0.15	-3.22		0.08	-8.51		0.08	-15.13		0.15
125	CO2-eq	-0.03		0.11	-3.23		0.11	-8.69		0.11	-15.51	x	0.11
126	CO2-eq	-0.10		0.10	-3.30		0.10	-8.60		0.10	-15.30		0.10
127	CO2-eq	0.07	x	0.05	-3.43	x	0.05	-8.78	x	0.05	-15.57	x	0.05
128	CO2-eq	-0.37	x	0.08	-3.58	x	0.08	-8.97	x	0.08	-15.58	x	0.08
129	CO2-eq	-0.08		0.05	-3.30		0.08	-8.65		0.09	-15.14		0.08
131	CO2-eq	-0.26	x	0.01	-3.45	x	0.02	-8.80	x	0.03	-15.47	x	0.06
132	CO2-eq	-0.13		0.05	-3.33		0.05	-8.72		0.05	-15.38		0.05
133	-	-		-	-		-	-		-	-		-
136	CO2-eq	-0.43	x	0.15	-3.64		0.20	-8.96		0.20	-15.54		0.21
137	CO2-eq	0.10	x	0.06	-3.20		0.04	-8.57		0.06	-15.32		0.07

These data arrived after the deadline and were not compiled									
112	CO2-eq	-0.17	0.14	-3.02	0.11	-8.70	0.14	-15.30	0.10
134	CO2-eq	-0.20	0.09	-3.1	0.05	-8.46	0.06	-15.36	0.08

Table 1, part 2/2: The results of δ18O analyses of four intercomparison samples (OH-1, OH-2, OH-3, OH-4) and the associated standard uncertainty, as reported by the laboratories participating in the interlaboratory comparison. Symbols (#) and (x) mark the results rejected in the first and second step of the statistical treatment, respectively.

Lab. ID no.	Preparation method	IC-OH-1			IC-OH-2			IC-OH-3			IC-OH-4		
		dD vs. VSMOW [‰]		±1 sigma	dD vs. VSMOW [‰]		±1 sigma	dD vs. VSMOW [‰]		±1 sigma	dD vs. VSMOW [‰]		±1 sigma
10	Zn, 500°C	-4.1		0.6	-31.0		0.7	-61.1		0.7	-109.0		0.9
12	Cr	-12.1	#	0.5	-37.9	#	0.5	-65.2	x	0.5	-111.0	x	0.5
13	Cr, 800°C	-2.7		0.7	-29.5		1.0	-60.1		0.8	-107.9	x	0.4
14	Cr	-3.6		0.2	-30.8		0.7	-61.0		1.0	-109.1		0.6
15	Zn, 700°C	-0.3	x	0.4	-30.7		0.9	-63.4	x	0.8	-112.9	x	1.5
16	Cr, 750°C	-4.1		0.8	-31.0		0.8	-61.3		0.8	-110.1		0.8
17	-	-		-	-		-	-		-	-		-
19	U	-4.1		0.5	-31.0		0.5	-61.1		0.5	-109.4		0.5
21	U, 850°C	-4.6	x	0.3	-31.9	x	0.3	-61.3		0.3	-109.7		0.3
22	-	-		-	-		-	-		-	-		-
24	-	-		-	-		-	-		-	-		-
25	Mn, 900°C	-3.4		1.5	-31.7		1.5	-63.5		1.5	-110.9		1.5
26	Zn	-3.1		0.9	-31.4		0.9	-61.5		0.9	-109.3		0.9
27	-	-		-	-		-	-		-	-		-
28	Zn	-4.0		1.0	-30.9		1.0	-61.3		1.0	-109.5		1.0
29	Zn, 500°C	-8.4		3.0	-33.3		3.0	-63.6		3.0	-108.3		3.0
31	Zn	-4.0		2.0	-33.0		2.0	-64.0		2.0	-112.0		2.0
32	-	-		-	-		-	-		-	-		-
33	Pt - eq.	-4.0		2.0	-32.0		3.0	-60.0		2.0	-110.0		2.0
34a	Zn	-4.3		2.7	-29.4		1.9	-62.7		2.0	-111.9		1.3
34b	Pt - eq.	-2.0		1.2	-28.9	x	0.8	-62.7		1.2	-110.9		1.5
35	Zn, 500°C	-18.0	#	2.8	-37.5	#	3.6	-66.5		4.4	-113.5		2.5
36	Pt - eq.	-3.9		0.4	-31.1		0.7	-61.9		0.7	-109.3		0.6
39	Pt - eq.	-2.0		1.9	-24.9	#	6.1	-58.3		6.8	-114.4		7.1
42	Zn	-3.5		1.0	-31.5		1.0	-62.0		1.0	-112.0		1.5
43	Zn	-2.2		0.9	-29.6		0.7	-59.9		1.5	-107.8		1.2
44	Cr, 910°C	-4.0		0.5	-30.7		0.5	-60.4		0.5	-108.2	x	0.5
45	Zn	-6.2		1.8	-32.0		3.3	-61.7		2.9	-108.6		2.1
46	-	-		-	-		-	-		-	-		-
47	Pt - eq.	-5.1		0.8	-32.2		0.8	-62.4		0.8	-110.9		0.8
51	-	-		-	-		-	-		-	-		-
52	Zn	-4.0		1.2	-32.0		1.2	-63.0		1.2	-108.0		1.2
53	Pt - eq.	-4.2		0.6	-30.9		0.6	-61.1		0.5	-109.2		0.4
54	Pt - eq.	-4.3		0.5	-31.3		0.5	-61.2		0.5	-109.6		0.5
55	-	-		-	-		-	-		-	-		-
58	U	-4.3		0.6	-31.0		0.7	-61.4		0.7	-109.7		0.5
61	Zn	-0.2	x	1.5	-28.6		1.5	-62.0		1.5	-109.8		1.5
62	-	-		-	-		-	-		-	-		-
64	Pt - eq.	-5.7	x	0.8	-32.1		0.8	-63.0	x	0.8	-110.4		0.9
65	Zn	-3.1		1.2	-31.1		1.2	-61.5		1.2	-109.0		1.2
67a	Zn, 480°C	-7.4	x	1.0	-32.4		1.0	-63.0		1.0	-110.9		1.0
67b	Cr, 850°C	-7.5	x	0.5	-32.7	x	0.5	-63.2	x	0.5	-111.2	x	0.5
68	Cr,800°C	-3.0		0.5	-30.6		0.5	-60.4		0.5	-109.6		0.6
69	-	-		-	-		-	-		-	-		-

Table 2, part 1/2:The results of δ^2H analyses of four intercomparison samples (OH-1, OH-2, OH-3, OH-4) and the associated standard uncertainty, as reported by the laboratories participating in the interlaboratory comparison. Symbols (#) and (x) mark the results rejected in the first and second step of the statistical treatment, respectively.

Lab. ID no.	Preparation method	IC-OH-1 dD vs. VSMOW [‰]		±1 sigma	IC-OH-2 dD vs. VSMOW [‰]		±1 sigma	IC-OH-3 dD vs. VSMOW [‰]		±1 sigma	IC-OH-4 dD vs. VSMOW [‰]		±1 sigma
		continuation of table from the previous page											
71	Cr	-5.1	x	0.4	-31.7		0.5	-62.2	x	0.3	-110.3	x	0.3
72	Zn, 480°C	-6.6		1.5	-33.8		1.5	-63.3		1.5	-110.8		1.5
73	U	-4.8	x	0.2	-30.1		0.9	-62.7		1.1	-110.3		1.5
75	Pt - eq.	-4.5		0.8	-32.0	x	0.5	-61.7		0.9	-109.8		0.9
78	Zn, 480°C	-2.8		1.0	-29.7		1.0	-61.0		1.0	-110.3		1.0
79	Zn	-4.3		0.6	-31.8		0.7	-61.5		0.7	-110.1		0.9
82	Zn, 700°C	-4.1		1.0	-31.6		1.0	-61.5		1.0	-110.0		1.0
83	Zn, 450°C	-4.6		1.1	-31.1		1.1	-61.0		0.8	-109.4		1.2
85	Zn, 450°C	-9.2	x	2.2	-36.0	x	1.5	-67.0	x	1.7	-116.6	#	4.7
86	Zn	-4.2		0.5	-31.4		0.5	-61.3		0.5	-109.4		0.5
88	Zn	-6.7		1.8	-33.5		2.1	-65.4		2.1	-112.0		2.0
89	Zn	-4.6		1.3	-30.9		1.3	-61.6		1.3	-110.1		1.3
93	Pt - eq.	-4.1		1.6	-30.8		0.8	-60.3		1.8	-108.3		1.1
94	Zn, 500°C	-3.8		0.8	-31.2		0.5	-61.4		0.7	-109.7		1.0
96	Zn, 500°C	-1.8		2.0	-29.5		2.0	-58.8		2.0	-108.9		2.0
97	Pt - eq.	-5.4		1.0	-32.2		1.0	-62.3		1.5	-110.8		1.8
99	Zn, 500°C	-6.1		1.4	-32.9		1.4	-66.5	x	1.4	-115.5	x	1.4
101	Zn	-1.3		1.7	-32.3		1.6	-58.1	x	1.4	-115.3	x	1.1
105	GC	-24.0	#	0.8	-51.5	#	1.6	-85.6	#	2.3	-133.3	#	3.1
106	Pt - eq.	-6.3		5.7	-30.3		6.5	-58.7		4.3	-107.4		4.2
107	U	-3.0		3.0	-34.0		3.0	-62.4		3.0	-108.5		3.0
108	Pt - eq.	-3.8		1.0	-32.0		1.0	-60.8		1.0	-110.1		1.0
109		-4.0		0.6	-32.8	x	0.6	-61.6		0.6	-106.6	x	0.6
111	Pt - eq.	-3.0		1.0	-30.5		1.0	-61.4		1.0	-108.9		1.0
113	Zn	-4.4		1.1	-30.4		0.5	-60.3		1.3	-105.6	x	1.7
114	Pt - eq.	-3.9		1.0	-30.7		1.0	-60.3		1.0	-108.7		1.0
115	Cr	-6.0	x	0.1	-33.8	x	0.2	-64.9	x	0.3	-113.4	x	0.5
116	U	-3.9		0.6	-31.1		0.7	-60.7		0.6	-109.3		0.7
117	Zn	-4.5		0.8	-31.7		1.0	-61.5		1.0	-110.1		1.2
118	Zn	-4.0		2.0	-31.9		2.0	-72.1	#	2.0	-113.2		2.0
121	Pt - eq.	-4.0		2.0	-31.3		2.0	-60.1		2.0	-109.1		2.0
122	Pt - eq.	-2.5	x	0.3	-30.1		0.5	-60.7		0.6	-109.5		0.6
123	Zn, 500°C	-0.2	x	0.4	-28.9	x	0.2	-59.8		1.0	-107.8		2.5
125	Zn	-2.8		1.4	-31.1		1.4	-62.3		1.4	-109.4		1.4
126	Cr	-4.8		1.0	-31.8		1.0	-61.2		1.0	-109.0		1.0
127	Cr, 800°C	-0.8	x	1.0	-30.7		1.0	-60.5		1.0	-108.4		1.0
128	-	-		-	-		-	-		-	-		-
129	Zn	-1.9	x	0.4	-32.2	x	0.6	-60.4		0.7	-109.4		0.7
131	Zn	-4.0		0.4	-30.6		1.0	-60.8		0.4	-108.9		0.4
132	Pt - eq.	-3.4		1.1	-30.6		1.1	-60.5		1.1	-109.7		1.1
133	Zn, 480°C	-8.5	x	1.1	-31.2		1.7	-60.1		1.6	-103.1	#	1.9
136	Zn, 450°C	-2.7		1.2	-30.0		1.1	-58.6	x	1.1	-110.3		1.3
137	Zn, 450°C	-5.4		1.3	-32.3		0.9	-62.5	x	0.4	-110.9		1.0

These data arrived after the deadline and were not included in the compilation									
112	-	-	-	-	-	-	-	-	-
134	Zn	-0.6	1.0	-28.7	0.7	-59.9	0.8	-106.2	1.0

Table 2, part 2/2: The results of δ^2H analyses of four intercomparison samples (OH-1, OH-2, OH-3, OH-4) and the associated standard uncertainty, as reported by the laboratories participating in the interlaboratory comparison. Symbols (#) and (x) mark the results rejected in the first and second step of the statistical treatment, respectively.

For oxygen-18 analyses, the CO_2 equilibration method was used by almost all participating laboratories. The conversion of water to hydrogen gas for deuterium measurements was done using one of the following methods: (i) reduction of water using granulate zinc (38 labs), (ii) reduction of water over hot uranium (6 labs), (iii) reduction of water over hot chromium (11 labs), and (iv) equilibration with H_2 using Pt as catalyst (18 labs) and (v) manganese reduction (1 lab).

3. STATISTICAL EVALUATION OF THE RESULTS

The statistical analysis of the submitted results was undertaken with two major objectives in mind:

- obtaining best estimates (consensus values) for the ^{18}O and ^{2}H content in the distributed samples as well as the standard uncertainty of these derived consensus values.
- assessing the performance of individual laboratories (precision and accuracy) with respect to the adopted consensus $\delta^{18}O$ and $\delta^{2}H$ values for the analysed samples.

To reach this goal, a two-stage statistical treatment, adopted in previous interlaboratory exercises of similar a nature (Rozanski et al., 1992; Araguàs-Araguàs and Rozanski, 1995), was applied separately for the subset of results originating from the selected group of laboratories and for the entire population of the submitted results.

<u>The two-stage statistical treatment:</u>
In stage I of the statistical treatment, obvious outliers were discarded based on the frequency distribution of values: after determination of the upper (H_U) and lower (H_L) quartiles, as well as the interquartile range (H_U-H_L), the values exceeding $H_U + 3.0\cdot(H_U-H_L)$ and falling below $H_L - 3.0\cdot(H_U-H_L)$ were discarded. The values discarded in stage I are marked with #-symbol in Tables 1 and 2. The provisional mean after stage I is further used in the stage II outlier rejection procedure.

In stage II of the evaluation process, the remaining results were assessed through examination of the difference between each reported isotope result *x* and the provisional mean *m* of stage I, divided by the standard uncertainty *s* quoted by the given laboratory. The results for which the ratio $|(x-m)|/s$ was larger than 2 were discarded. This procedure identifies those results which are not homogenous with the rest of the analysed population.

In the final step, the weighted average (eq. 1) was calculated by weighing the remaining individual results by the reciprocal of the quoted variance and the standard uncertainty was calculated with eq. 2:

$$X_W = \frac{\sum_{i=1}^{n} \frac{x_i}{s_i^2}}{\sum_{i=1}^{n} \frac{1}{s_i^2}} \qquad (1)$$

$$stdev = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)}{(n-1)}} \qquad (2)$$

The estimated standard uncertainty of the mean (ese) was calculated according to the following formula

$$ese(X_W) = \frac{s_W}{\sqrt{\left(\sum_{i=1}^{n} \frac{1}{s_i^2}\right)}} \qquad (3)$$

with

$$s_w^2 = \frac{\sum_{i=1}^{n} \frac{(x_i - X_w)^2}{s_i^2}}{n-1} \qquad (4)$$

where *n* stands for the final number of results accepted after the second step of the data evaluation procedure.

Application of the two-stage statistical treatment on different data sets:
This two stage evaluation process was first applied on the subset of results submitted by the group of selected laboratories (Lab ID. No. 10, 13, 19, 32, 58, 109 and 111; ID No. 10 identifies the IAEA Isotope Hydrology Laboratory): Here the provisional *median* of the results after stage I is used in stage II instead of the provisional *mean*, since the number of laboratories *n* is smaller than 10. In stage II the weighted mean values (Table 3) and their standard uncertainties were calculated for each sample according to equations (1) and (2).
These weighted means of the subgroup of selected laboratories represent the adopted consensus values of the four samples (Table 5). The estimated standard uncertainty of the mean (ese) was calculated for each sample according to equation (3) and (4).

Results from selected laborities in the intercomparison exercise

Sample	Original data median / range (reported values)	After removal of outliers (stage I & II) weighted mean ± stdev (accepted values)
delta O-18	[‰] vs. VSMOW	[‰] vs. VSMOW
OH - 1	-0.07 / 0.12 (7)	-0.05 ± 0.03 (6)
OH - 2	-3.27 / 0.07 (7)	-3.28 ± 0.03 (7)
OH - 3	-8.67 / 0.17 (7)	-8.65 ± 0.06 (6)
OH - 4	-15.31 / 0.12 (7)	-15.28 ± 0.03 (6)
delta D		
OH - 1	-4.1 / 1.6 (6)	-3.9 ± 0.9 (6)
OH - 2	-31.0 / 3.3 (6)	-30.8 ± 0.9 (5)
OH - 3	-61.2 / 1.5 (6)	-61.3 ± 0.3 (5)
OH - 4	-109.0 / 3.1 (6)	-109.4 ± 0.6 (4)

Table 3: The calculated standard deviations (stdev) are multiplied with an appropriate correction factor *f* , since the number of observations *n* is smaller than 10 (micro statistical group). The used correction factors *f(n)* are *f*(4) = 1.62, *f*(5)= 1.42, *f*(6) = 1.31 and *f*(7) = 1.25.

Secondly, the evaluation process was applied to the entire population of the results (Table 4). The arithmetic mean value of the results remaining after stage I was adopted as a preliminary mean for stage II of the data evaluation process (m–value). Then, the weighted mean values and the associated standard uncertainties were calculated for each sample.

Results from all participating laboratories in the intercomparison excercise

Sample	Original data mean ± stdev (reported values)	After removal of outliers (stage I & II) weighted mean ± stdev (accepted values)
delta O-18	[‰] vs. VSMOW	[‰] vs. VSMOW
OH - 1	-0.10 ± 0.21 (80)	-0.11 ± 0.10 (61)
OH - 2	-3.33 ± 0.23 (80)	-3.30 ± 0.13 (59)
OH - 3	-8.68 ± 0.20 (80)	-8.69 ± 0.11 (55)
OH - 4	-15.34 ± 0.20 (80)	-15.33 ± 0.11 (58)
delta D		
OH - 1	-4.2 ± 2.0 (74)	-4.1 ± 1.3 (56)
OH - 2	-31.5 ± 1.8 (75)	-31.3 ± 1.0 (64)
OH - 3	-61.8 ± 2.1 (75)	-61.4 ± 1.4 (62)
OH - 4	-110.0 ± 2.1 (75)	-109.8 ±1.4 (62)

Table 4: Summary statistics of the results obtained by all laboratories participating in the exercise. Weighted means were calculated according to eq.(1) and the standard deviation was calculated according to eq.(2).

Third, the evaluation process was performed again on the entire population, but this time the adopted consensus value was used in the stage II outlier criterion instead of the provisional mean of all laboratories. This procedure allows to identify the outliers in the intercomparison exercise according to the adopted consensus values. The values discarded in this evaluation procedure are marked with x-symbol in Tables 1 and 2.

Consensus value of the four intercomparison water samples

Sample	consensus value	estimated standard uncertainty of the mean (ese) for the adopted consensus values
delta O-18	[‰] vs. VSMOW	[‰] vs. VSMOW
OH - 1	-0.05	0.01
OH - 2	-3.28	0.01
OH - 3	-8.65	0.02
OH - 4	-15.28	0.01
delta D		
OH - 1	-3.9	0.2
OH - 2	-30.8	0.2
OH - 3	-61.3	0.1
OH - 4	-109.4	0.2

Table 5: The adopted consensus δ-values for the analysed water samples (column 2) derived from the results submitted by the group of seven selected laboratories. The estimated standard uncertainties of the mean (ese) for the adopted consensus values (column 3) were calculated according to eq.(3) and (4).

4. SUMMARY TABLES AND FIGURES

Table 1 and 2 list the results of the $\delta^{18}O$ and $\delta^{2}H$ determinations performed on four intercomparison samples (OH-1, OH-2, OH-3, OH-4) and the associated standard uncertainty, as reported by the laboratories participating in the interlaboratory comparison. Symbols (#) and (x) mark the results rejected in the first and second step of statistical treatment, respectively, using the consensus values.

Table 3 summarises the results obtained for the selected group of seven laboratories, which were assigned to provide the consensus values for the analysed set of samples. In the second column, the median and the range of the results submitted by this group is reported. In the third column, the weighted mean (eq.1) and the associated standard uncertainty is reported, both calculated after removal of outliers (Stage I & II).

Table 4 provides analogous statistics for the entire population of the submitted results (including the group of seven selected laboratories).

In Table 5, the adopted consensus δ-values for the analysed water samples are reported together with the estimated standard uncertainty of the mean (ese) for these consensus values, calculated using equations (1) and (2).

It is apparent from Tables 4 and 5 that the weighted mean values obtained from statistical evaluation of the entire population of the submitted results deviate systematically from the adopted consensus values. This shift towards more negative δ-values amounts to ca. –0.04 ‰ for $\delta^{18}O$ and –0.3 ‰ for $\delta^{2}H$. One possible explanation for this apparent discrepancy is discussed in the conclusions.

Lab. ID.Nr.	Preparation method	deviation with respect to the dO-18 consensus value [‰] vs. VSMOW OH-1	OH-2	OH-3	OH-4	total deviation [‰]
10	CO2-eq	0.01	0.01	0.05	0.01	0.08
12	CO2-eq	0.25	0.18	0.05	0.08	0.56
13	CO2-eq	0.01	0.00	0.01	0.01	0.03
14	CO2-eq	-0.15	-0.82	-0.35	-0.42	1.74
15	CO2-eq	-0.08	-0.05	-0.04	-0.02	0.19
16	CO2-eq	-0.17	-0.10	-0.09	-0.04	0.40
17	CO2-eq	-0.04	-0.09	-0.12	-0.20	0.46
19	CO2-eq	0.03	0.03	-0.02	-0.05	0.12
21	CO2-eq	-0.85	-0.12	0.05	0.28	1.30
22	CO2-eq	0.11	0.01	-0.21	-0.48	0.81
24	CO2-eq	-0.05	-0.05	0.05	-0.04	0.19
25	CO2-eq	-0.30	-0.24	-0.20	-0.07	0.81
26	CO2-eq	0.00	0.10	-0.04	0.05	0.19
27	CO2-eq	-0.10	-0.02	-0.04	-0.03	0.18
28	CO2-eq	-0.12	-0.14	-0.15	-0.04	0.45
29	CO2-eq	0.05	-0.32	0.05	-0.22	0.64
31	CO2-eq	0.00	0.03	-0.01	-0.06	0.10
32	CO2-eq	-0.03	-0.04	-0.09	-0.03	0.19
33	CO2-eq	-0.25	-0.22	-0.25	-0.32	1.04
34a	CO2-eq	0.03	0.17	0.13	0.08	0.41
35	CO2-eq	0.09	0.11	0.12	0.17	0.49
36	CO2-eq	-0.04	0.12	0.04	0.08	0.28
39	CO2-eq	-0.02	-0.11	-0.23	-0.39	0.75
42	CO2-eq	-0.19	-0.15	-0.21	-0.21	0.76
43	CO2-eq	0.04	0.12	0.18	0.02	0.36
44	CO2-eq	-0.02	0.09	0.07	0.03	0.21
45	CO2-eq	0.56	0.57	0.85	0.78	2.76
46	CO2-eq	-0.04	-0.02	-0.03	-0.08	0.17
47	CO2-eq	-0.15	-0.22	-0.15	-0.02	0.54
51	CO2-eq	0.05	-0.70	-0.28	-0.21	1.24
52	CO2-eq	-0.10	-0.02	-0.20	-0.17	0.49
53	CO2-eq	-0.03	-0.01	-0.02	-0.04	0.10
54	CO2-eq	0.00	0.06	0.04	-0.01	0.10
55	CO2-eq	0.04	0.02	0.04	0.01	0.10
58	CO2-eq	-0.02	0.01	-0.02	-0.02	0.07
61	CO2-eq	-0.09	-0.08	-0.02	0.06	0.26
62	CO2-eq	-0.02	-0.08	-0.02	-0.06	0.18
64	CO2-eq	-0.17	-0.15	-0.12	-0.11	0.55
65	CO2-eq	0.04	0.08	0.08	0.12	0.32
67a	CO2-eq	0.03	0.03	-0.02	-0.04	0.12
68	CO2-eq	0.07	0.07	0.04	0.01	0.19
69	CO2-eq	-0.21	-0.21	-0.30	-0.37	1.10

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Table 6, part 1/2: The devitions of the reported values with respect to the adopted consensus values for Oxygen-18. The last coulumn contains the sum of the absolute values of the deviations (total).

Lab. ID.No	Preparation method	Deviation with respect to the dO·18 consensus value [‰] vs. VSMOW OH-1	OH-2	OH-3	OH-4	total deviation [‰]
	continuation of table 6 from previous page					
71	CO2-eq	-0.08	0.13	0.16	0.11	0.48
72	CO2-eq	0.06	0.03	0.12	-0.01	0.21
73	Hydrochloride	-0.15	0.48	0.65	0.38	1.66
75	CO2-eq	-0.18	-0.06	-0.03	-0.07	0.34
78	CO2-eq	-0.03	-0.04	-0.07	-0.10	0.24
79	CO2-eq	-0.11	-0.15	-0.09	-0.16	0.51
82	CO2-eq	-0.03	-0.02	-0.03	-0.03	0.11
83	CO2-eq	-0.18	-0.19	-0.22	-0.15	0.74
85	CO2-eq	0.64	0.63	0.43	0.23	1.93
86	CO2-eq	0.19	0.17	0.14	0.07	0.57
88	CO2-eq	-0.13	-0.07	0.04	-0.02	0.26
93	CO2-eq	-0.26	-0.19	-0.24	-0.26	0.95
96	CO2-eq	-0.06	-0.05	-0.06	-0.07	0.24
97	CO2-eq	0.09	0.11	0.08	0.05	0.33
99	CO2-eq	0.00	-0.01	-0.01	0.01	0.04
101	CO2-eq	-0.01	0.08	0.34	0.40	0.83
105	GC	-3.25	-3.32	-3.45	-2.72	12.74
106	CO2-eq	-0.76	-0.83	-0.67	-0.60	2.86
107	CO2-eq	-0.40	-0.44	-0.31	-0.26	1.41
108	CO2-eq	0.05	0.01	0.00	-0.04	0.10
109	CO2-eq	-0.09	0.01	-0.12	-0.11	0.32
111	CO2-eq	-0.02	-0.03	-0.02	-0.04	0.11
113	CO2-eq	-0.11	-0.19	-0.01	-0.10	0.41
114	CO2-eq	-0.17	-0.17	-0.23	-0.20	0.77
115	CO2-eq	0.04	0.00	0.02	-0.11	0.17
116	CO2-eq	-0.12	-0.08	-0.08	-0.07	0.35
117	CO2-eq	-0.12	-0.13	-0.08	0.04	0.38
121	CO2-eq	0.00	0.03	-0.02	-0.05	0.10
122	CO2-eq	0.50	0.41	0.13	-0.09	1.12
123	CO2-eq	-0.12	0.06	0.14	0.15	0.47
125	CO2-eq	0.02	0.05	-0.04	-0.23	0.34
126	CO2-eq	-0.05	-0.02	0.05	-0.02	0.14
127	CO2-eq	0.12	-0.15	-0.13	-0.29	0.69
128	CO2-eq	-0.32	-0.30	-0.32	-0.30	1.24
129	CO2-eq	-0.03	-0.02	0.00	0.14	0.20
131	CO2-eq	-0.21	-0.17	-0.15	-0.19	0.72
132	CO2-eq	-0.08	-0.05	-0.07	-0.10	0.30
136	CO2-eq	-0.38	-0.36	-0.31	-0.26	1.31
137	CO2-eq	0.15	0.08	0.08	-0.04	0.34
These data arrived after the deadline and were not included in the compilation						
112	CO2-eq	-0.12	0.26	0.05	0.02	0.39
134	CO2-eq	0.25	0.18	0.19	0.12	0.74

Table 6, part 2/2: The devitions of the reported values with respect to the adopted consensus values for Oxygen-18. The last coulumn contains the sum of the absolute values of the deviations (total).

Lab. ID.Nr.	Preparation method	Deviation with respect to the consensus value [‰] vs. VSMOW				total deviation [‰]
		OH-1	OH-2	OH-3	OH-4	
10	Zn, 500°C	-0.2	-0.2	0.2	0.4	1.0
12	Cr	-8.2	-7.1	-3.9	-1.6	20.8
13	Cr, 800°C	1.2	1.3	1.2	1.5	5.2
14	Cr	0.3	0.0	0.3	0.3	0.9
15	Zn, 700°C	3.5	0.1	-2.1	-3.5	9.2
16	Cr, 750°C	-0.2	-0.2	0.0	-0.7	1.1
19	U	-0.2	-0.2	0.2	0.0	0.6
21	U, 850°C	-0.7	-1.1	0.0	-0.3	2.1
25	Mn, 900°C	0.5	-0.9	-2.2	-1.5	5.0
26	Zn	0.8	-0.6	-0.2	0.1	1.7
28	Zn	-0.1	-0.1	0.0	-0.1	0.3
29	Zn, 500°C	-4.5	-2.5	-2.3	1.1	10.5
31	Zn	-0.1	-2.2	-2.7	-2.6	7.6
33	Pt	-0.1	-1.2	1.3	-0.6	3.2
34a	Zn	-0.4	1.4	-1.4	-2.5	5.7
34b	Pt - eq.	1.9	1.9	-1.4	-1.5	6.7
35	Zn, 500°C	21.9	-6.7	-5.2	-4.1	30.1
36	H2-eq.	0.0	-0.2	-0.6	0.1	1.0
39	H2 - eq.	1.9	5.9	3.0	-5.0	15.7
42	Zn	0.4	-0.7	-0.7	-2.6	4.4
43	Zn	1.7	1.2	1.4	1.6	5.9
44	Cr, 910°C	-0.1	0.1	0.8	1.2	2.2
45	Zn	-2.3	-1.2	-0.4	0.8	4.8
47	Pt - eq.	-1.2	-1.4	-1.1	-1.5	5.2
52	Zn	-0.1	-1.2	-1.7	1.4	4.5
53	Pt - eq.	-0.3	-0.1	0.2	0.3	0.9
54	Pt-eq.	-0.4	-0.5	0.1	-0.2	1.2
58	U	-0.4	-0.2	-0.1	-0.3	1.0
61	Zn	3.7	2.2	-0.7	-0.4	7.0
64	Pt-eq.	-1.8	-1.3	-1.7	-1.0	5.8
65	Zn	0.7	-0.3	-0.2	0.4	1.6
67a	Zn, 480°C	-3.6	-1.6	-1.7	-1.4	8.3
67b	Cr, 850°C	-3.6	-1.9	-1.9	-1.7	9.2
68	Cr, 800°C	0.9	0.2	0.9	-0.2	2.1

table 7 is contiued on next page

Table 7, part 1/2: Deviations of reported values with respect to the adopted consensus value for deuterium. The last column contains the sum of the absolute values of the departures (total).

Lab. ID.Nr.	Preparation method	Deviation with respect to the consensus value [‰] vs. VSMOW OH-1	OH-2	OH-3	OH-4	total deviation [‰]
continuation of table 7 from previous page						
71	Cr	-1.2	-0.9	-0.9	-0.9	3.9
72	Zn, 480°C	-2.7	-3.0	-2.0	-1.4	9.1
73	U	-0.9	0.7	-1.4	-0.9	3.9
75	Pt-eq.	-0.6	-1.2	-0.4	-0.4	2.6
78	Zn, 480°C	1.1	1.1	0.3	-0.9	3.3
79	Zn	-0.4	-1.0	-0.2	-0.7	2.3
82	Zn, 700°C	-0.2	-0.8	-0.2	-0.5	1.7
83	Zn, 450°C	-0.7	-0.3	0.3	0.0	1.3
85	Zn, 450°C	-5.3	-5.2	-5.7	-7.2	23.4
86	Zn	-0.3	-0.6	0.0	0.0	1.0
88	Zn	-2.8	-2.7	-4.1	-2.6	12.2
89	Zn	-0.7	-0.1	-0.3	-0.6	1.7
93	Pt - eq.	-0.2	0.0	1.0	1.1	2.3
94	Zn, 500°C	0.1	-0.4	-0.1	-0.3	0.9
96	Zn, 500°C	2.0	1.3	2.5	0.6	6.4
97	Pt - eq.	-1.5	-1.4	-1.0	-1.4	5.4
99	Zn, 500°C	-2.2	-2.1	-5.2	-6.1	15.6
101	Zn	2.6	-1.5	3.2	-5.9	13.1
105	GC	-20.1	-20.7	-24.3	-23.9	89.0
106	Pt.-eq.	-2.4	0.5	2.6	2.0	7.5
107	U	0.9	-3.2	-1.1	0.9	6.1
108	Pt-eq.	0.1	-1.2	0.5	-0.7	2.4
109	Zn, 500°C	-0.1	-2.0	-0.3	2.8	5.3
111	Pt - eq.	0.9	0.3	-0.1	0.5	1.8
113	Zn	-0.5	0.4	1.0	3.9	5.7
114	Pt - eq.	0.0	0.1	0.9	0.7	1.8
115	Cr	-2.1	-3.0	-3.6	-4.0	12.7
116	U	-0.1	-0.2	0.6	0.1	1.0
117	Zn	-0.6	-0.9	-0.2	-0.7	2.4
118	Zn	-0.1	-1.1	-10.8	-3.8	15.8
121	Pt - eq.	-0.1	-0.5	1.1	0.3	2.1
122	Pt - eq.	1.4	0.8	0.6	-0.1	2.9
123	Zn, 500°C	3.7	1.9	1.5	1.6	8.7
125	Zn	1.1	-0.3	-1.0	0.0	2.4
126	Cr	-0.9	-1.0	0.1	0.4	2.4
127	Cr, 800°C	3.0	0.1	0.8	1.0	4.9
129	Zn	2.0	-1.4	0.9	0.0	4.3
131	Zn	-0.1	0.2	0.5	0.5	1.3
132	Pt - eq.	0.5	0.2	0.7	-0.3	1.7
133	Zn, 480°C	-4.6	-0.4	1.2	6.3	12.5
136	Zn, 450°C	1.2	0.9	2.7	-0.9	5.6
137	Zn, 450°C	-1.5	-1.5	-1.2	-1.5	5.7

This data arrived after the deadline and were not included in the compilation						
134	Zn	3.3	2.1	1.4	3.2	10.0

Table 7, part 2/2: Deviations of the reported values with respect to the adopted consensus value for deuterium. The last column contains the sum of the absolute values of the departures (total).

In Tables 6 and 7 the departures of reported values with respect to the adopted consensus values for oxygen-18 and deuterium are presented for all analysed samples. The last column in both tables contains the sum of the departures (absolute values) for the given isotope and for each participating laboratory.

Figures 1.1 to 1.8 show the $\delta^{18}O$ and δD results with the associated standard uncertainties as provided by each laboratory for samples OH-1 to OH-4. The laboratory identification numbers were sorted according to the reported δ-values: from more negative to more positive (S-shape plots). In order to keep all plots consistent with a constant range of δ-values, some outliers were only partly plotted or not shown at all. The solid horizontal line indicates the adopted consensus value (Table 5, second column). The dashed line represents the mean value as derived for the entire population of the results after removal of outliers (Table 4, third column) with the standard deviation indicated by the two dotted lines.

Figures 2.1. to 2.4. show the $\delta^{18}O$ - $\delta^{2}H$ plots for the results submitted by the participating laboratories, for the samples OH-1 to OH-4, respectively. The indicated error bars represent the standard deviation of the initial data set of the two groups before the outlier rejection procedure: the two groups are ‘all labs’ (Table 4, second column: only lab 105 is already rejected as obvious outlier) and the ‘seven selected labs’ (Table 3, second column).

Figures 3.1 and 3.2. illustrate the distribution of the calculated departures of the measured $\delta^{18}O$ and $\delta^{2}H$ values with respect to the adopted consensus values. Laboratory identification numbers have been sorted according to increasing cumulative departures.

Figures 4.1 and 4.2 present the absolute cumulative departures for $\delta^{18}O$ and $\delta^{2}H$, respectively, for each laboratory participating in the exercise.

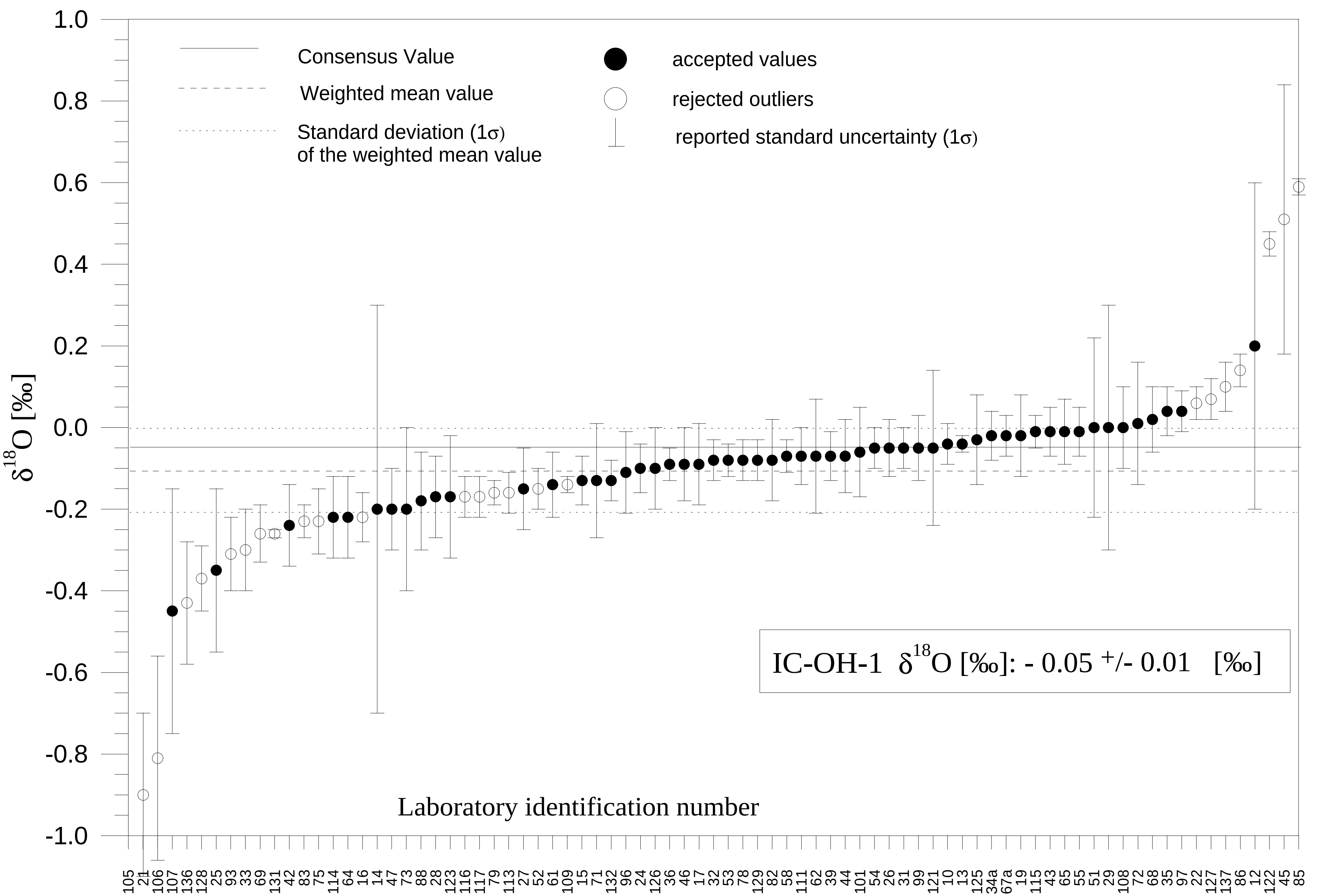


Figure 1.1: S-shape plots of $\delta^{18}O$ results for the sample OH-1 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

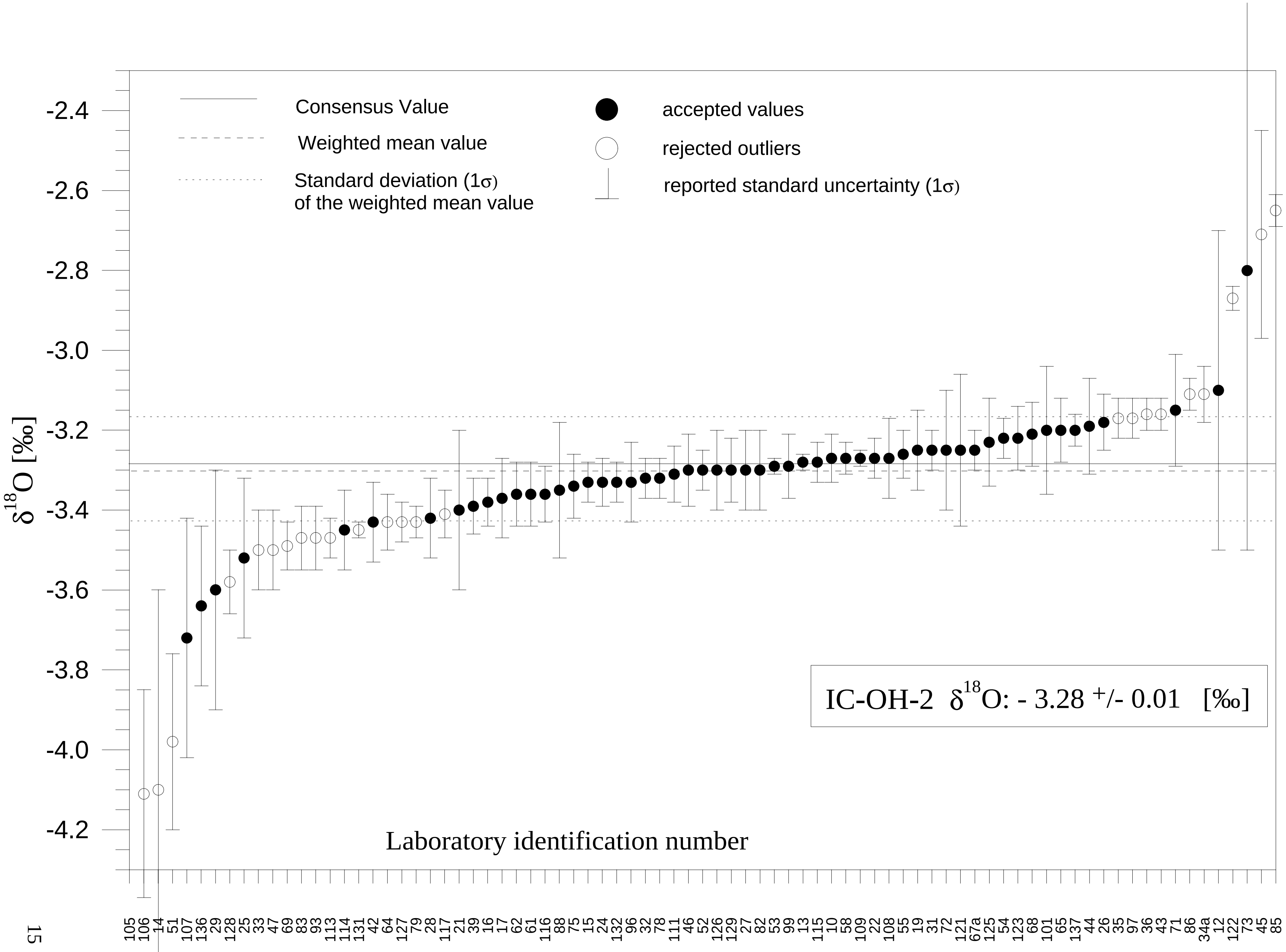


Figure 1.2: S-shape plots of $\delta^{18}O$ results for the sample OH-2 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

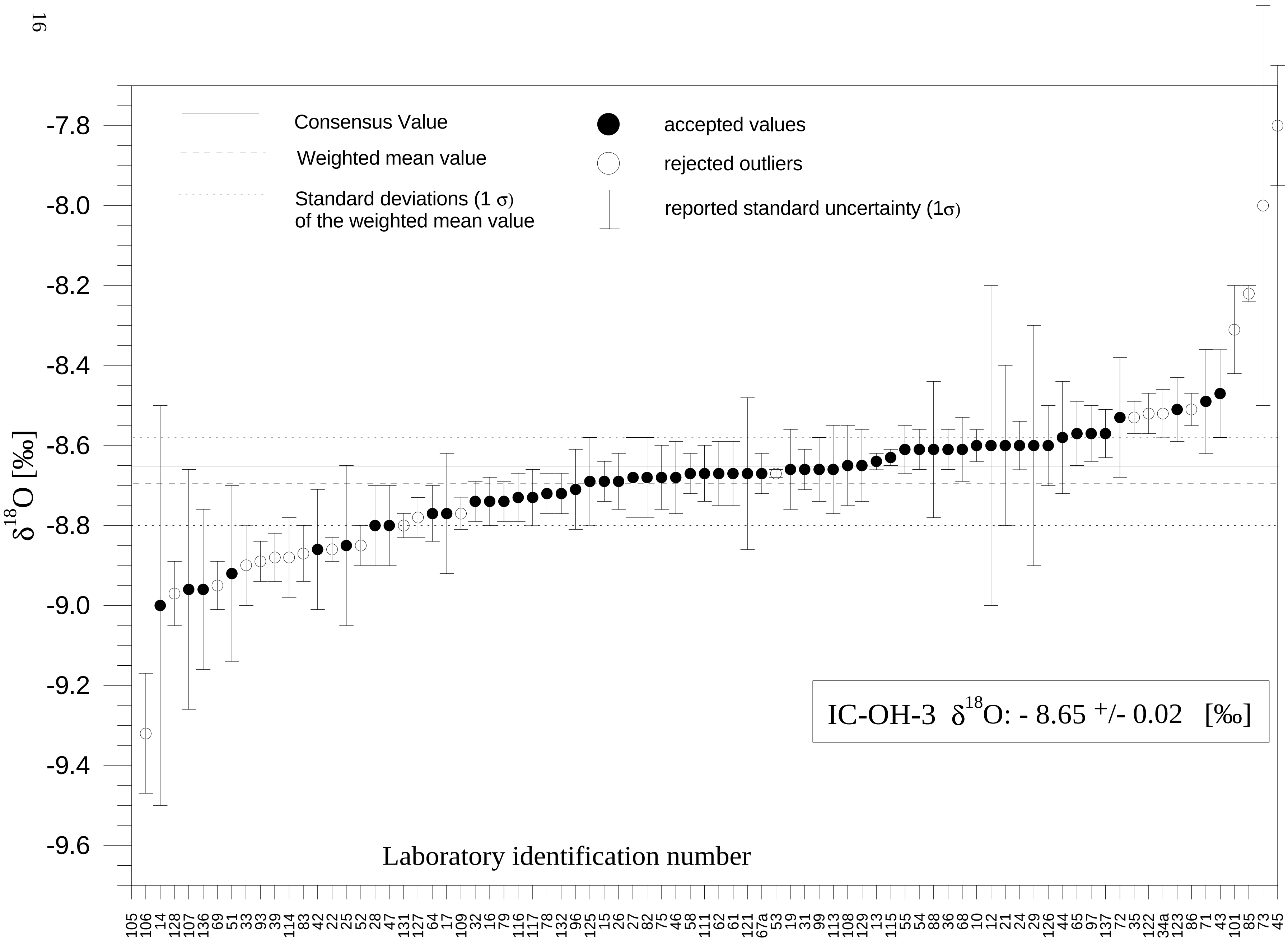


Figure 1.3: S-shape plots of $\delta^{18}O$ results for the sample OH-3 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

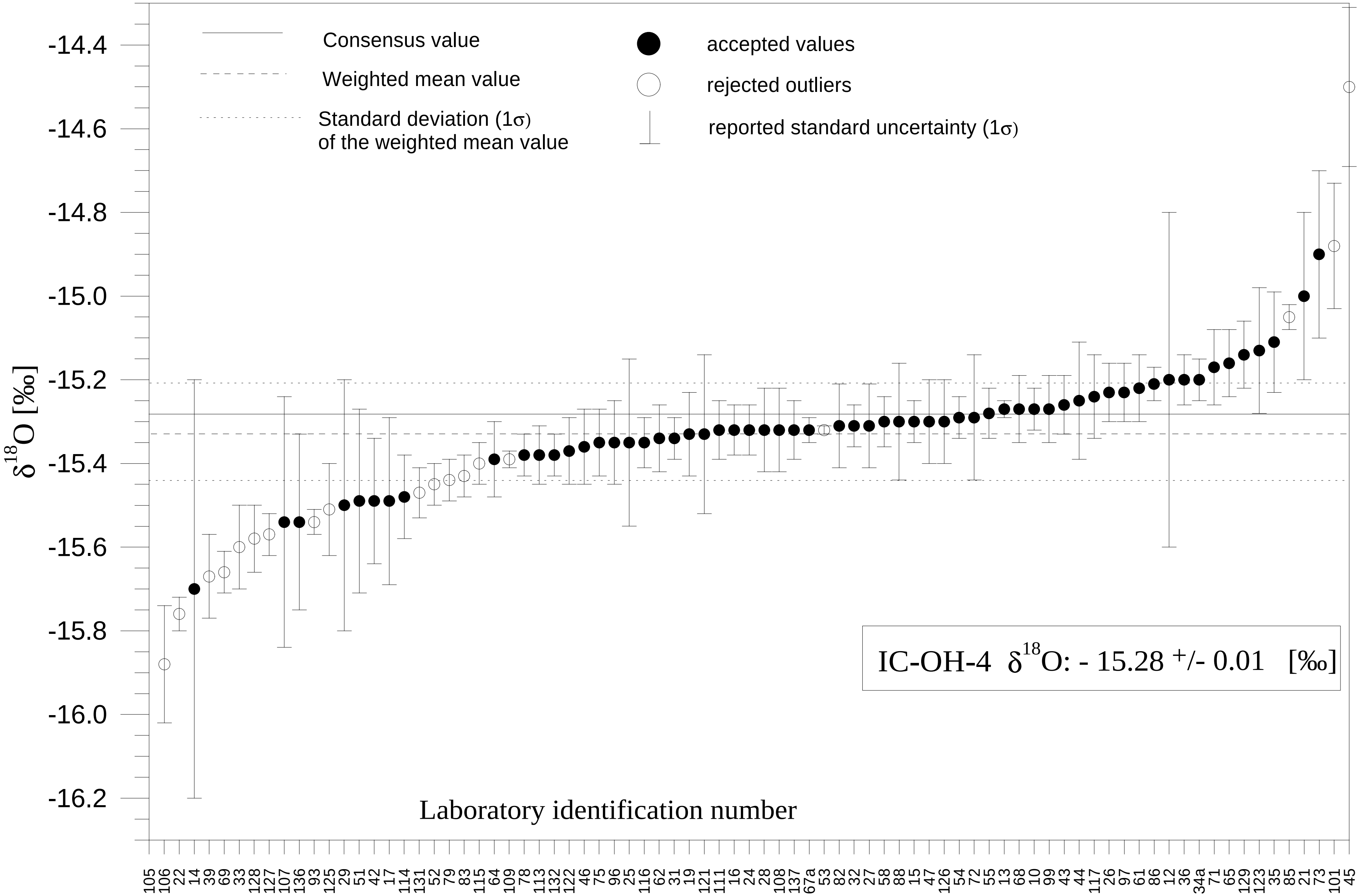


Figure 1.4: S-shape plots of $\delta^{18}O$ results for the sample OH-4 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

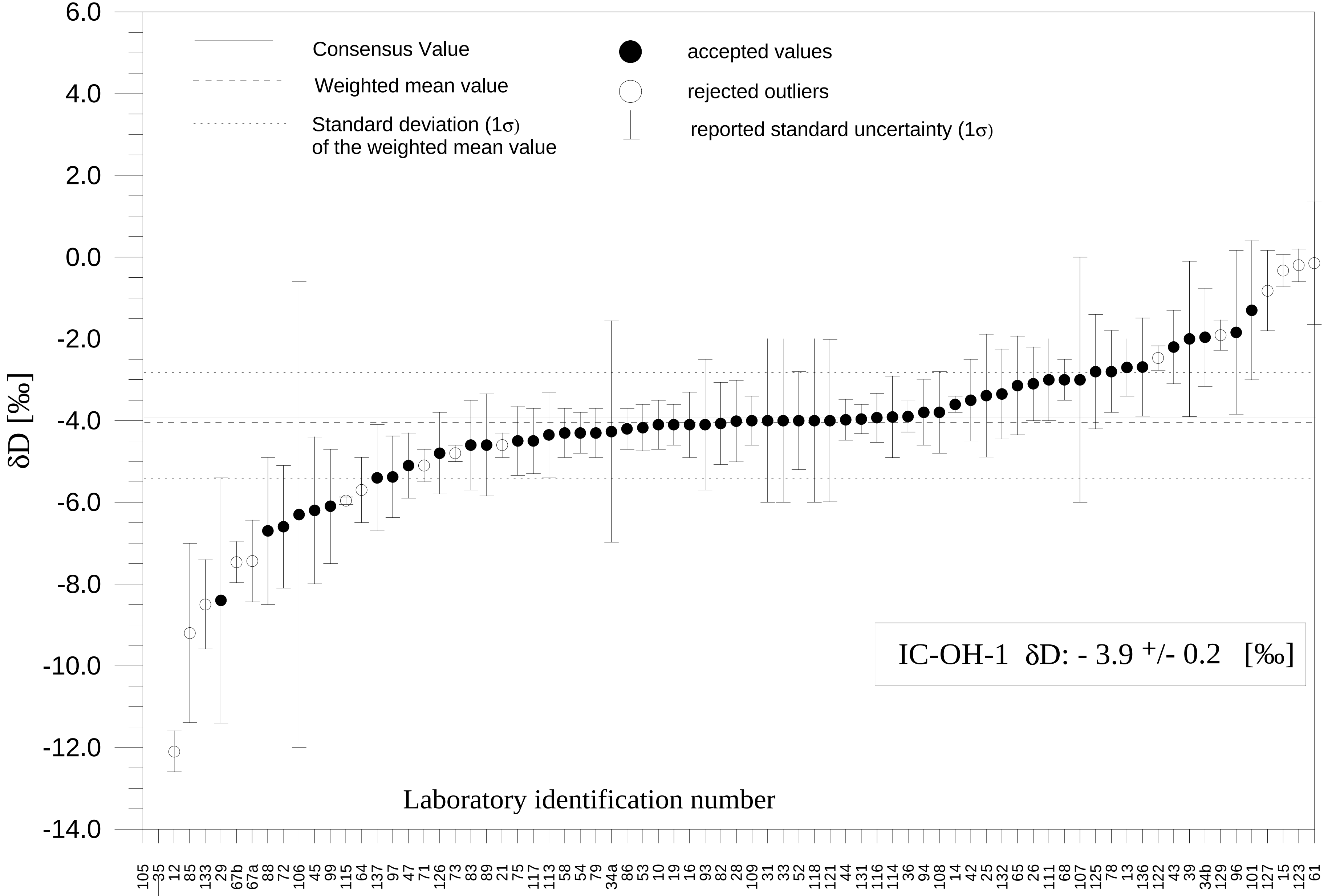


Figure 1.5: S-shape plots of δ^2H results for the sample OH-1 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

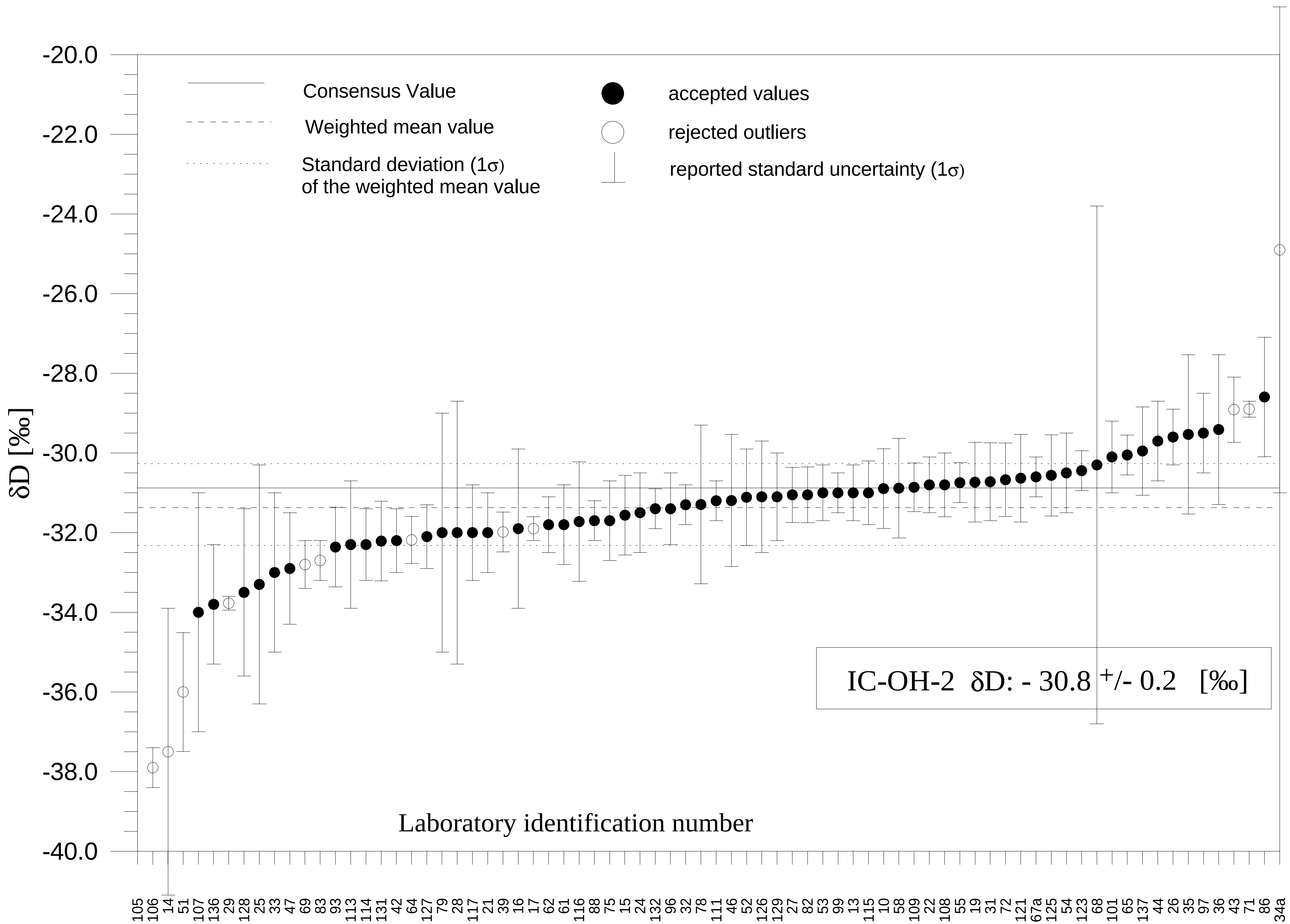


Figure 1.6: S-shape plots of δ^2H results for the sample OH-2 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

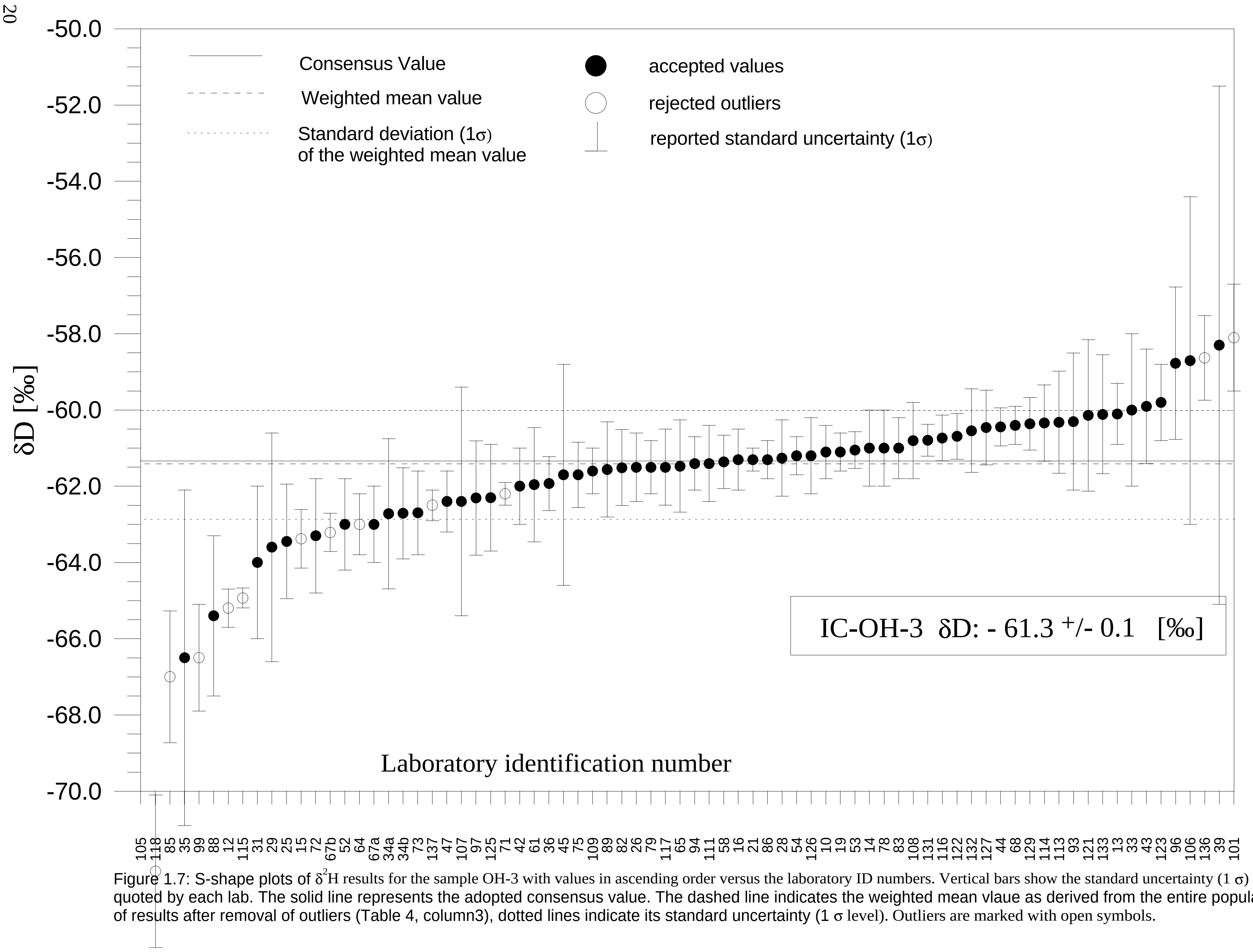


Figure 1.7: S-shape plots of δ^2H results for the sample OH-3 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

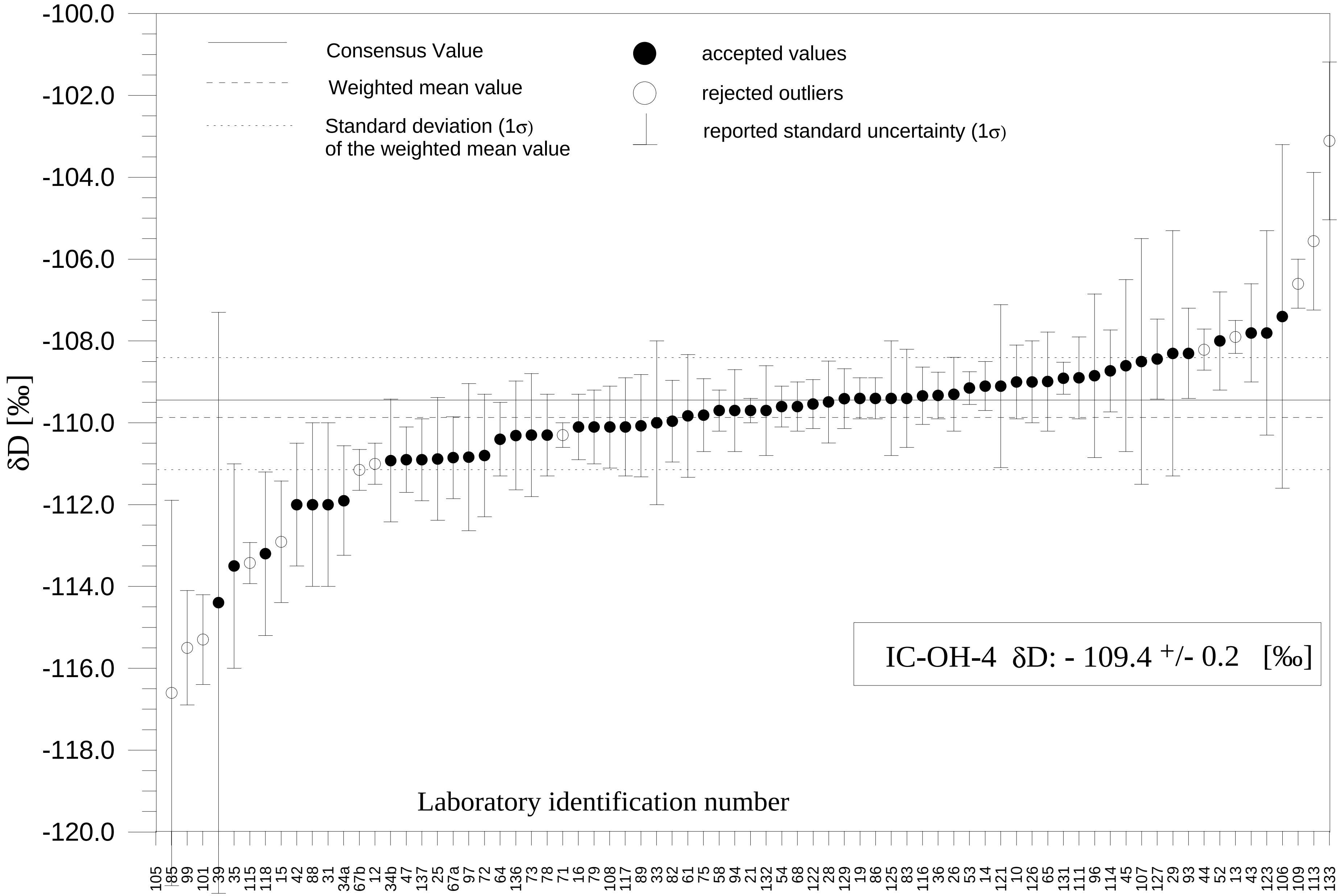


Figure 1.8: S-shape plots of δ^2H results for the sample OH-4 with values in ascending order versus the laboratory ID numbers. Vertical bars show the standard uncertainty (1 σ) quoted by each lab. The solid line represents the adopted consensus value. The dashed line indicates the weighted mean vlaue as derived from the entire population of results after removal of outliers (Table 4, column3), dotted lines indicate its standard uncertainty (1 σ level). Outliers are marked with open symbols.

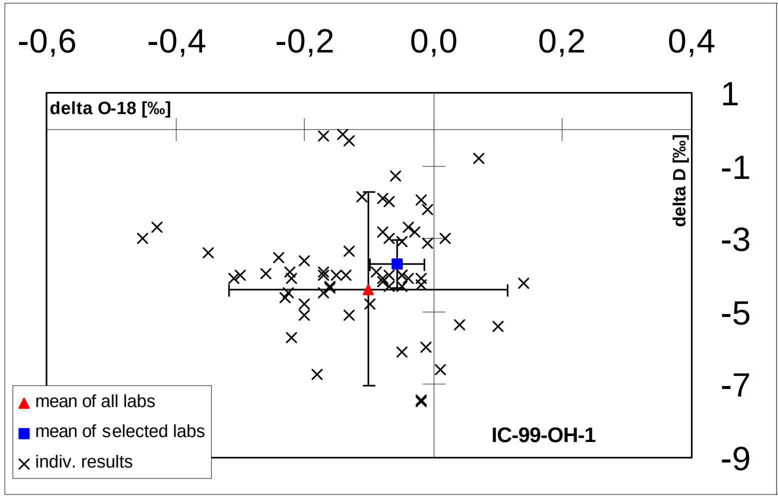


Figure: 2.1: δD versus δ^{18}O: results of OH-1

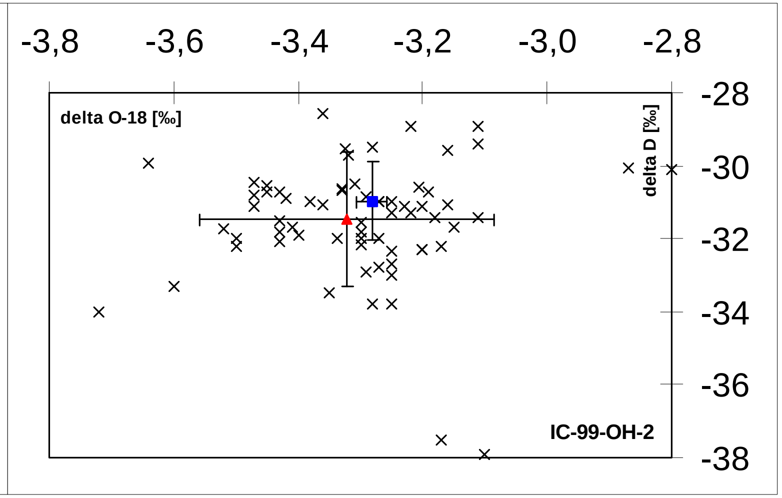


Figure: 2.2: δD versus δ^{18}O: results of OH-2

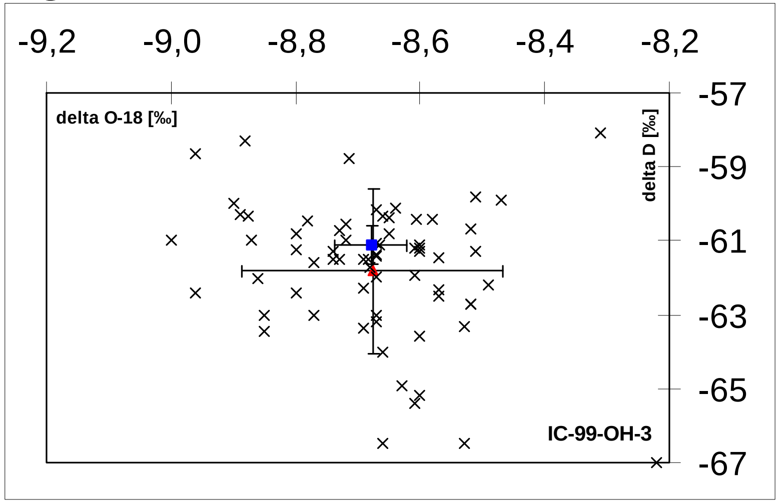


Figure: 2.3: δD versus δ^{18}O: results of OH-3

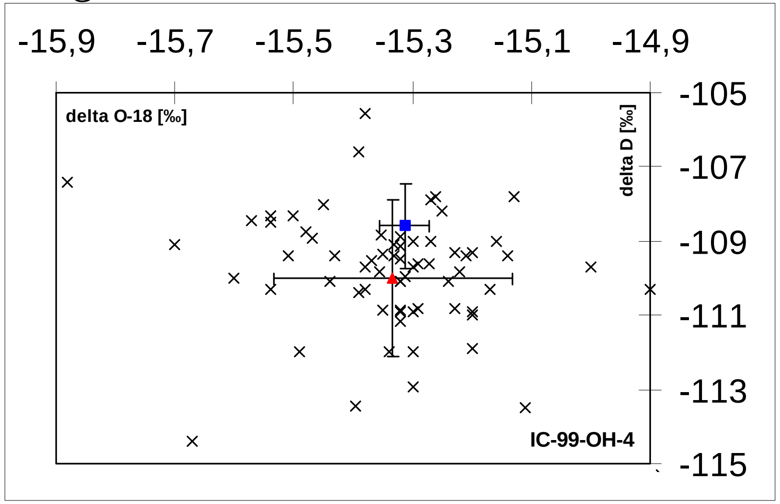


Figure: 2.4: δD versus δ^{18}O: results of OH-4

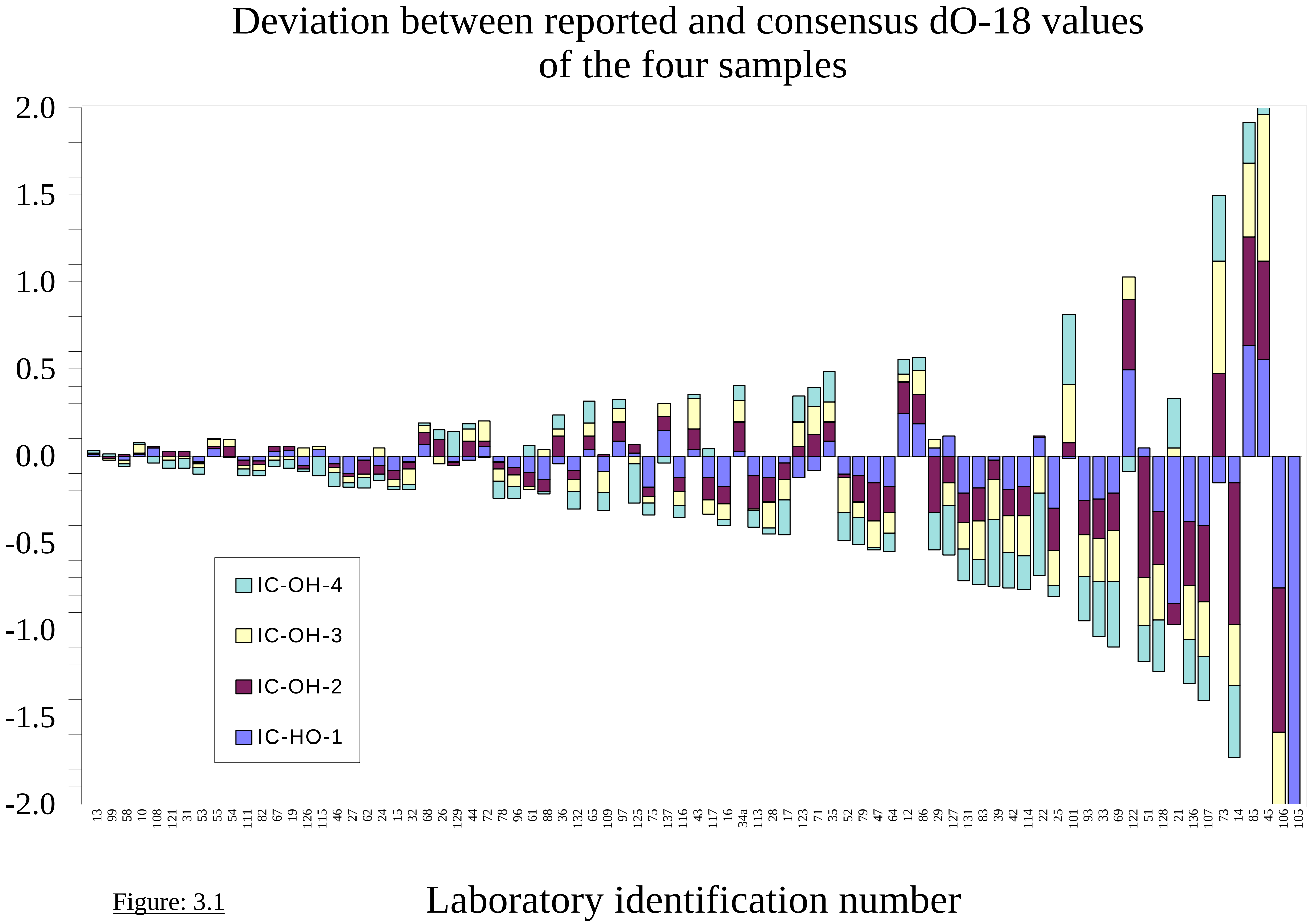

Deviation between reported and consensus dO-18 values
of the four samples
Deviation of dO-18 [‰ vs. VSMOW]
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
IC-OH-4
IC-OH-3
IC-OH-2
IC-HO-1
13 99 58 10 108 121 31 53 55 54 111 82 67 19 126 115 46 27 62 24 15 32 68 26 129 44 72 78 96 61 88 36 132 65 109 97 125 75 137 116 43 117 16 34a 113 28 17 123 71 35 52 79 47 64 12 86 29 127 131 83 39 42 114 22 25 101 93 33 69 122 51 128 21 136 107 73 14 85 45 106 105
Laboratory identification number

Figure: 3.1

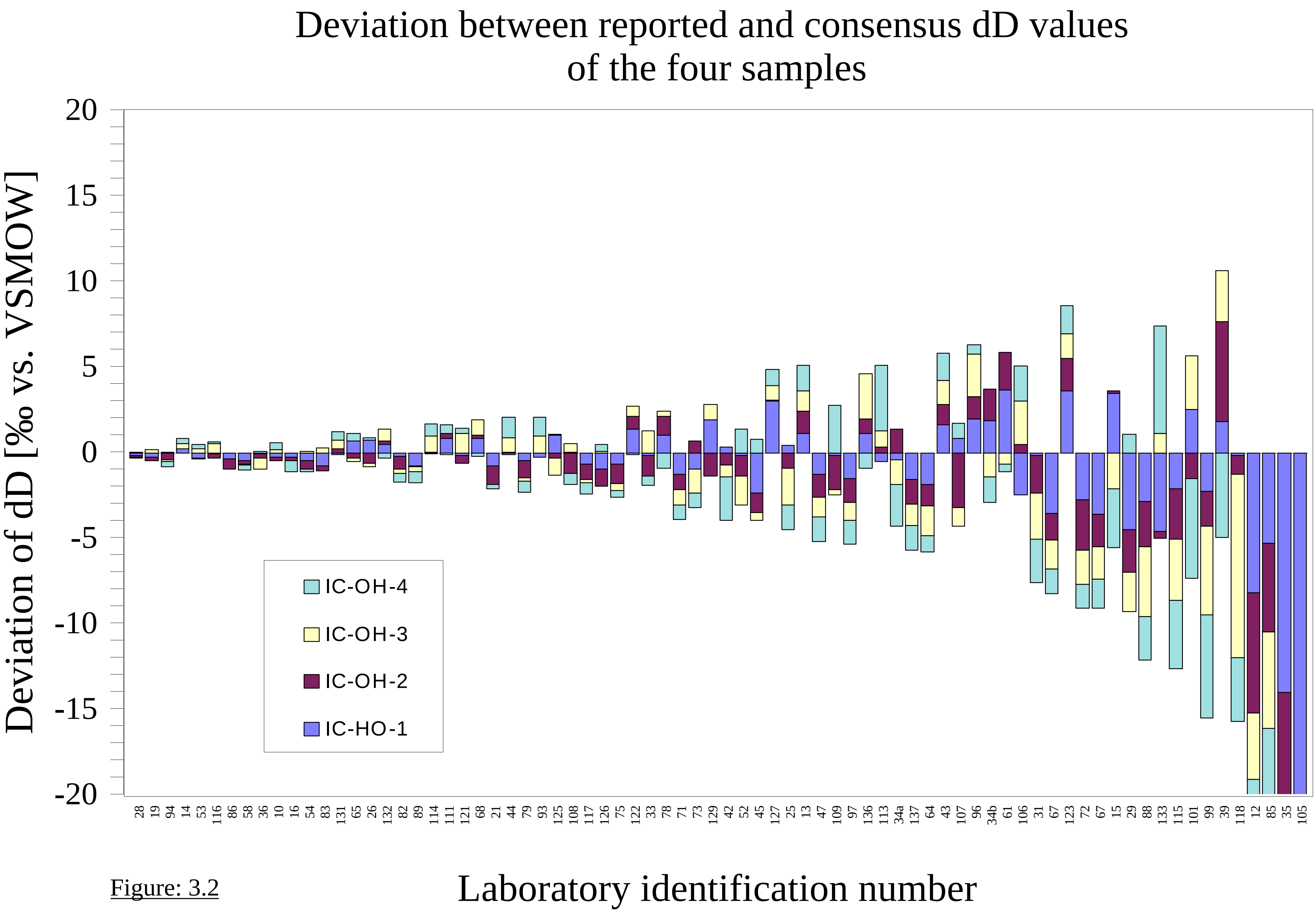

Deviation between reported and consensus dD values
of the four samples
Deviation of dD [‰ vs. VSMOW]
20
15
10
5
0
-5
-10
-15
-20
IC-OH-4
IC-OH-3
IC-OH-2
IC-HO-1
28 19 94 14 53 116 86 58 36 10 16 54 83 131 65 26 132 82 89 114 111 121 68 21 44 79 93 125 108 117 126 75 122 33 78 71 73 129 42 52 45 127 25 13 47 109 97 136 113 34a 137 64 43 107 96 34b 61 106 31 67 123 72 67 15 29 88 133 115 101 99 39 118 12 85 35 105
Laboratory identification number

Figure: 3.2

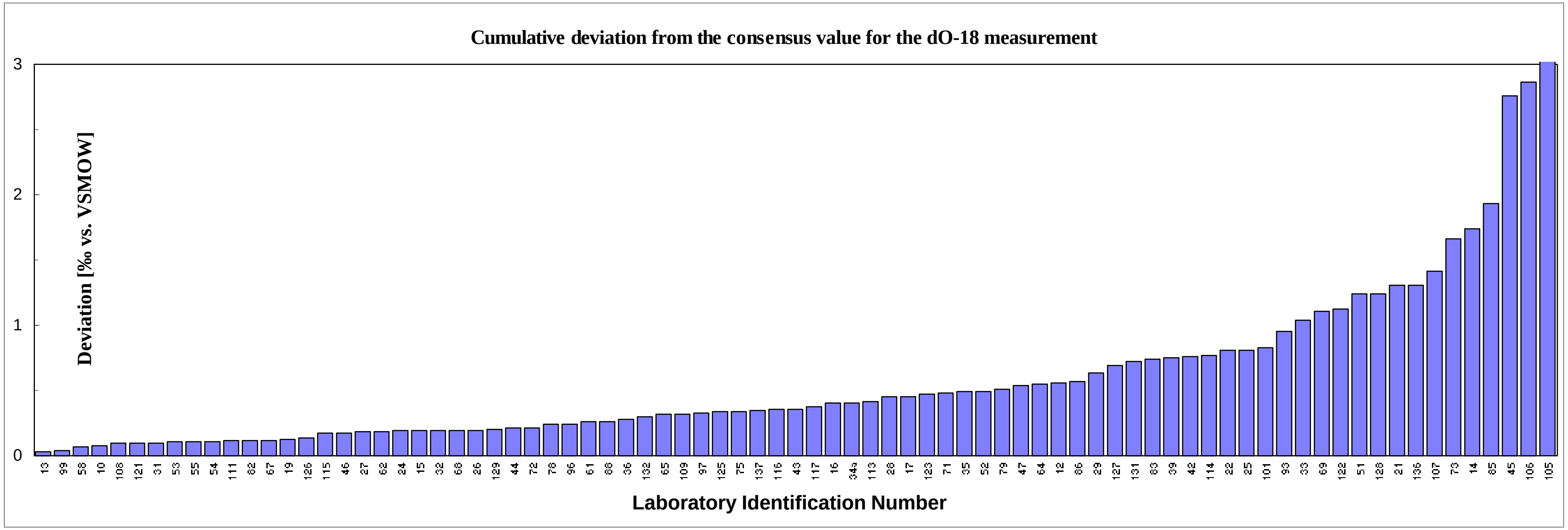
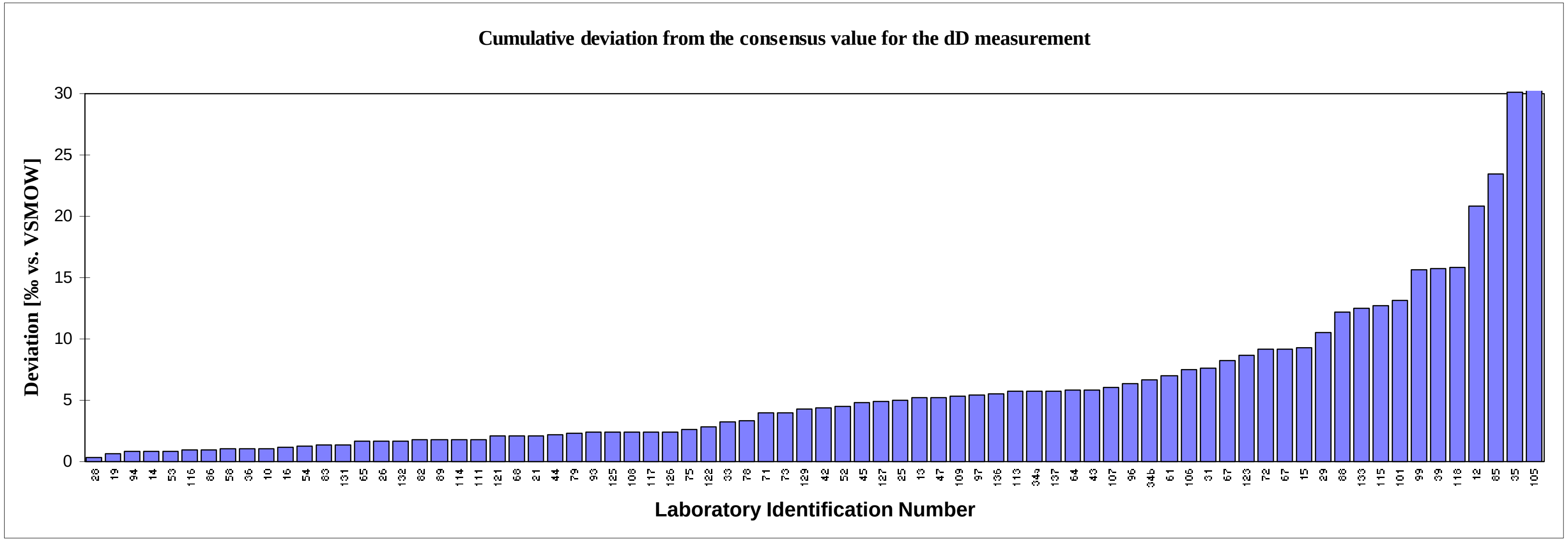


Figure 4.1 and Figure 4.2: Cumulative deviation from the consensus values for all four $\delta^{18}O$ and $\delta^{2}H$ results of each laboratory. Laboratories are sorted according to increasing cumulative deviation from the consensus values.



5. CONCLUSIONS

More than 80 laboratories performing routine $\delta^{18}O$ and $\delta^{2}H$ analyses of water samples participated in the 2nd interlaboratory comparison test organised by the IAEA. They represent a substantial portion of the entire analytical community engaged in this type of measurements. Therefore, it is believed that the results of this test properly reflect the current situation with respect to accuracy and interlaboratory precision of stable isotope analyses of water samples. The following conclusions can be drawn on the basis of the results presented in this report:

The apparent interlaboratory precision (one-sigma level), derived from the whole pool of the analysed results, is in the order of 0.11 ‰ for $\delta^{18}O$ and 1.3 ‰ for $\delta^{2}H$ (Table 4, third column). Thus, in first instance no significant improvement of this performance indicator could be detected with respect to the 1st interlaboratory comparison in 1995. But if one takes into account the different general conditions in 1995 and in 1999 - in 1995 all participants were asked to calibrate their system with the attached ampoules of VSMOW/GISP/SLAP, in 1999 this was omitted - therefore the results can be interpreted as a slight improvement of the overall performance: In 1999 about 50% of the participants calibrated their internal standards during the exercise.
The above quoted values are similar to typical standard uncertainties reported by the majority of laboratories engaged in routine analysis of water samples (0.1 ‰ for $\delta^{18}O$ and 1.0 ‰ $\delta^{2}H$). Therefore, the conclusion drawn four years ago that these values set up practical limits for comparing the results originating from a large pool of different laboratories is still valid.

The apparent interlaboratory precision obtained for the group of seven selected laboratories was in the order of 0.04 ‰ for $\delta^{18}O$ and 0.8 ‰ for $\delta^{2}H$ (Table 3, third column).

Statistical analysis of the submitted results indicates that at least 25% of the laboratories participating in the exercise underestimate the standard uncertainty attached to their analyses and/or suffer from systematic effects of various nature (marked outliers).

No significant dependence of the obtained δ-values on the type of the sample preparation procedure could be detected. Although all values obtained with the GC-method have been rejected, this might not been interpreted by statistical methods since only one laboratory reported to perform this preparation procedure.

The results for the entire population are not normal distributed, which indicates non random systematic effects in a substantial subgroup of laboratories.
A small but nevertheless significant discrepancy in the reported results between the group of selected laboratories and the entire population of participants is identified. This shift towards more negative δ-values amounts to ca. –0.04 ‰ for $\delta^{18}O$ and –0.3 ‰ for $\delta^{2}H$ and pinpoints the importance of the applied calibration procedure (frequency, handling of primary standards, etc.) for the overall improvement of the precision and accuracy of the analysed water samples.
One possible explanation for the shift towards more negative values could be a slight evaporative enrichment of the used internal laboratory standards with time after the calibration against VSMOW (or evaporation of improperly stored VSMOW after initial opening of the glass ampoules, due to repeated use and/or leaky caps of a secondary storage container). It should be noted that evaporative loss of only 0.1% of the initial mass of the used internal standard or the VSMOW sample would be sufficient to explain the observed average isotope shift in the order of 0.04 ‰ for $\delta^{18}O$ and 0.3 ‰ for $\delta^{2}H$.

ACKNOWLEDGEMENTS

The efforts of all laboratories which participated in the 2nd IAEA interlaboratory comparison test and contributed with their results to the success of this exercise are highly appreciated. We would like to acknowledge the contribution of the group of selected laboratories which were instrumental in establishing the consensus δ values for the analysed waters, and in particular the involvement of Liliana Andreescu, Mira Gattin, Manfred Jaklitsch and Herbert Tatzber as staff members of the IAEA Isotope Hydrology Laboratory in preparation, calibration and shipment of the distributed water samples.

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ISOGEOCHEM newsgroup: http://geology.uvm.edu/geowww/isogeochem.html

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Fig.1.1.to 1.4. δ^{18}O values for samples OH-1 to OH-4 in ascending order, as reported by the participating laboratories. Vertical bars represent the standard uncertainty (one-sigma) quoted by each laboratory. The solid line represents the adopted consensus value (Table 5, second column). The dotted line represents the weighted mean value as calculated from the whole set of laboratories with the standard uncertainty (one sigma level) indicated by the two dotted lines.

Fig.1.5 to 1.8. δ^{2}H values for samples OH-1 to OH-4 in ascending order, as reported by the participating laboratories. Vertical bars represent the standard uncertainty (one-sigma) quoted by each laboratory. The solid line represents the adopted consensus value (Table 5, second column). The dotted line represents the weighted mean value as calculated from the whole set of laboratories with the standard uncertainty (one sigma level) indicated by the two dotted lines.

Figures 2.1. to 2.4. The δ^{18}O - δ^{2}H plots for the results submitted by the participating laboratories, for the samples OH-1 to OH-4, respectively. The indicated error bars represent the standard deviation (equ. 2) of the data of all labs (of the data of the selected labs, respectively) before the compilation procedure had been applied to the data sets.

Fig.3.1 and 3.2. Departures of the δ^{18}O and δ^{2}H values reported by the participating laboratories from the adopted consensus values. Laboratory identification numbers have been sorted according to increasing cumulative departures (absolute values).

Fig.4.1 and 4.2. Cumulative departures of the δ^{18}O and δ^{2}H values reported by the participating laboratories from the adopted consensus values (absolute values). Laboratories are sorted according to increasing value of this parameter.

Annex I

Participants in the 2nd IAEA intercomparison exercise
of stable isotopes in precipitation, 1999

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Annex II

Reporting Sheet
sent to all participants of the 2nd IAEA intercomparison exercise
of stable isotopes in precipitation, 1999
as attachment to the shipment
of the four water samples

2nd IAEA INTERLABORATORY COMPARISON
FOR STABLE ISOTOPE ANALYSES OF PRECIPITATION

Reporting Sheet

Lab ID No.: (Lab ID number is identical to the number stated on the sample bottles)

Participating Laboratory:

SAMPLE PREPARATION DATA*

Sample preparation technique (^{18}O) + Mass Spectrometer used:
Sample preparation technique (^{2}H) + Mass Spectrometer used:

*) describe briefly the method employed for sample preparation (e.g. zinc reduction for ^{2}H and CO_2 equilibration for ^{18}O) and the mass spectrometer (model type, 2 or 3 Faraday-cup-system) .

NORMALIZATION DATA**

Normalization procedure for ^{2}H: Date of last calibration using VSMOW/SLAP/GISP:
Normalization procedure for ^{18}O: Date of last calibration using VSMOW/SLAP/GISP:

**) describe briefly the procedure adopted in your laboratory to normalize the measured δ^{2}H and δ^{18}O values to the VSMOW-SLAP scale and state the isotopic composition of your calibrated laboratory standards.

FINAL RESULTS

SAMPLE	$\delta^{18}O_{VSMOW/SLAP}$ [$^{o}/_{oo}$]	Standard uncertainty# (one sigma)	Number of indiv. Analyses n(m)##	$\delta^{2}H_{VSMOW/SLAP}$ [$^{o}/_{oo}$]	Standard uncertainty# (one sigma)	Number of indiv. Analyses n(m)##	d-excess [$^{o}/_{oo}$]
IAEA-OH-**1**							
IAEA-OH-**2**							
IAEA-OH-**3**							
IAEA-OH-**4**							

EVALUATION OF UNCERTAINTY COMPONENTS#

a) ☐ by standard deviation of laboratory water standards.
b) ☐ by assessment of individual uncertainty components (state major ones):

Please note the remarks on Standard Uncertainty and Number of Analyses below before completing the form

#) Standard Uncertainty in table 'Final Results': This includes NOT ONLY the standard deviation of individual results of measurements of one sample. It rather means an assessment of all uncertainty components of the complete analysis procedure for the final result at your best knowledge (from the sample preparation: -e.g. temperature fluctuations of the equilibration bath- to the mass spectrometer: -variable isotope fractionation during gas transfer- and to the calculation: -assigned isotope values for the daily used laboratory water standard).

As a good approximation for the standard uncertainty in a laboratory one can use the standard deviation of individual results of a laboratory water standard over a reasonable period of time (two months, or more than 50 individual results). The standard uncertainty will often depend on the isotopic composition of the samples and may be larger for more negative δ-values. Please be aware that reporting of the 'one sigma' standard uncertainty is requested, so - for statisticians and QA officers - the coverage factor k is set to 1.

##) Number of Analyses in table 'Final Results': Please state the number analyses *n* used for calculation of the mean and the number of analyses rejected internally *m* in brackets, (e.g. 9(1) means total of ten analyses performed, nine taken to calculate mean values, one result rejected internally).

INDIVIDUAL ANALYSES

	$\delta^{18}O_{VSMOW/SLAP}$ [‰], individual determinations				$\delta^{2}H_{VSMOW/SLAP}$ [‰], individual determinations			
	IAEA-OH-1	IAEA-OH-2	IAEA-OH-3	IAEA-OH-4	IAEA-OH-1	IAEA-OH-2	IAEA-OH-3	IAEA-OH-4
1.								
2.								
3.								
4.								
5.								
6.								
7.								
8.								
9.								
10.								
add more								

Laboratory Manager................................

Date:...............................

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