COMMENT ON THE INTERNATIONAL ATOMIC ENERGY AGENCY REPORT ON THE ADVISORY GROUP MEETING ON STABLE ISOTOPE REFERENCE SAMPLES FOR GEOCHEMICAL AND HYDROLOGICAL INVESTIGATION, VIENNA, AUSTRIA, SEPTEMBER 19-21, 1983

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CONTENTS

	Page
Abstract	1
Introduction	1
Oxygen Isotope Fractionation Factor Between CO_2 and H_2O	2
Relationship Between the SMOW and PDB scales	6
Recommended $\delta^{18}O$ Value of NBS-19	6
Conclusions	7
References	8

ILLUSTRATIONS

		Page
Figure 1.	Revised figure 3 of Gonfiantini (1984) showing $\delta^{18}O$ conversion equations [modified from Friedman and O'Neil (1977) and from Gonfiantini (1984)]	4
Figure 2.	Figure 3 of Gonfiantini (1984) showing $\delta^{18}O$ conversion equations	5

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ABSTRACT

A report prepared by R. Gonfiantini summarizing the findings and recommendations of the 1983 Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrologic Investigations held in Vienna, September 19-21, 1983, does not accurately represent the consultants' consensus on three important points. The consultants (1) did not recommend the cited value of 1.04115 for the CO_2-H_2O oxygen isotope fractionation factor, (2) adopted a value of 1.0309 rather than 1.03086 to relate the PDB and SMOW scales, and (3) adopted a *firm* $\delta^{18}O$ value of -2.20 permil for NBS-19 on the PDB scale rather than agreeing that this would be a tentative value subject to modification when more measurements in selected laboratories are available.

INTRODUCTION

In September of 1983, the Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations convened in Vienna. This meeting was organized by the International Atomic Energy Agency (IAEA) and succeeded meetings on stable isotope reference standards held in 1966 and 1976.

The purpose of the Advisory Group Meeting was (1) to review in detail the results of reference samples analyzed since 1976, (2) to recommend preparation of new reference samples, and (3) to recommend guidelines for isotope reference standards and reporting of data by laboratories. A summary of the results, conclusions, and recommendations was prepared by R. Gonfiantini (1984), Scientific Secretary of the meeting.

The authors attended this meeting as IAEA consultants; furthermore, I. Friedman served as Chairman of this meeting. The report prepared by Gonfiantini (1984), differs from the group consensus on three important

recommendations. This report discusses these differences, which relate to oxygen isotope fractionation factors, the relationship between the SMOW and PDB scales, and the oxygen isotopic abundance of NBS-19.

The stable isotope standards discussed in this report are listed below.

Stable Isotope Reference Standards

Name	Abbreviation
National Bureau of Standards-19 (calcite)	NBS-19
Peedee Belemnite (calcite)	PDB
Standard Light Antarctic Precipitation	SLAP
Standard Mean Ocean Water	SMOW
Vienna-Standard Mean Ocean Water	V-SMOW

Stable isotope ratios are reported herein as a δ value relative to a standard, employing units of parts per thousand or permil. Therefore, for oxygen:

$$\delta^{18}O \text{ (in permil)} = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right] 1000$$

OXYGEN ISOTOPE FRACTIONATION FACTOR BETWEEN CO_2 AND H_2O

The partitioning of oxygen isotopes between two substances, A and B, is described by the isotopic fractionation factor α:

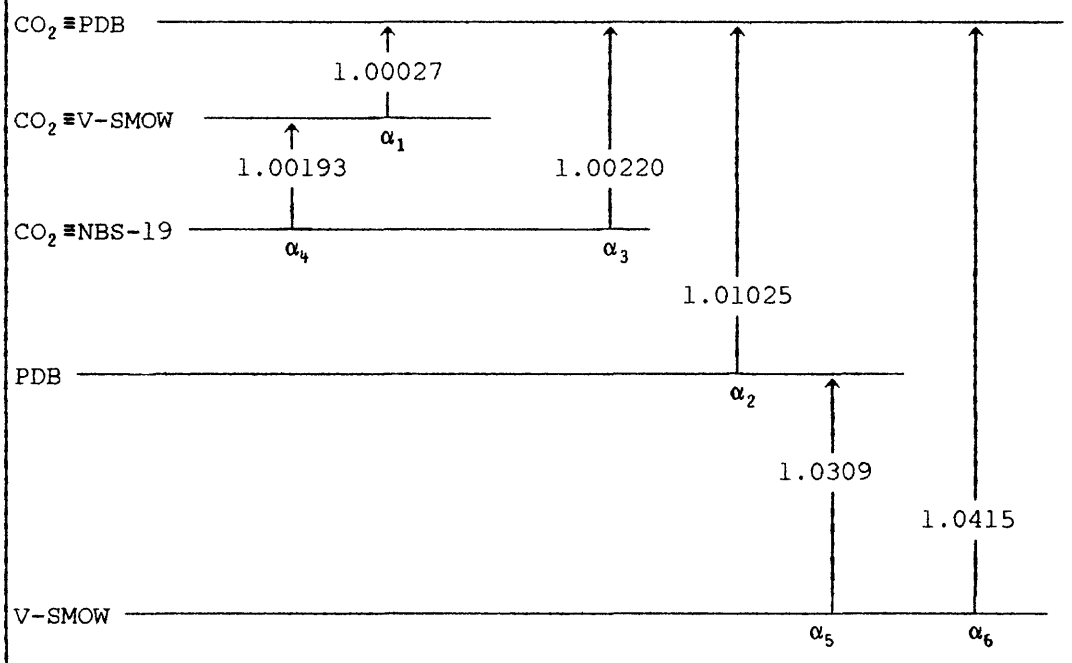
$$\alpha_{A-B} = \frac{(^{18}O/^{16}O)_A}{(^{18}O/^{16}O)_B}$$

where $(^{18}O/^{16}O)_A$ and $(^{18}O/^{16}O)_B$ are the oxygen isotope ratios in each substance.

Figure 1 illustrates the oxygen isotopic fractionation between CO_2≡PDB, CO_2≡V-SMOW, PDB, and V-SMOW. CO_2≡PDB is carbon dioxide liberated from PDB calcite and CO_2≡V-SMOW is carbon dioxide isotopically equilibrated with V-SMOW water.

Gonfiantini (1984) states on page 20, "For the oxygen-18 measurements in the water-calcite system, the fractionation factors recommended are those of fig. 3." Figure 2 herein is figure 3 of Gonfiantini (1984). The isotopic fractionation factor between CO_2≡V-SMOW and V-SMOW is the CO_2-H_2O isotope fractionation factor and in Gonfiantini (1984) is taken as 1.04115 at 25°C from work by Brenninkmeijer, Kraft, and Mook (1983). The group consensus was that this value of 1.04115 *should not* be preferred over other values in the literature (see Friedman and O'Neil, 1977) because most of the data used to calculate it were not normalized to V-SMOW/SLAP = -55.5 permil relative to V-SMOW. One exception is the value of 1.04120 revised from O'Neil and Epstein (1966) and reported by Friedman and O'Neil (1977). Because the consultants could not agree on a value of the CO_2-H_2O fractionation factor for adoption at this meeting, we have intentionally left it off figure 1.

On page 13, Gonfiantini (1984) states, "From the practical point of view, however, the normalized value of the fractionation factor between CO_2 and water should not differ significantly from that of 1.04115 proposed [at the 1983 meeting] by Mook (fig. 3)." The group consensus was that this was not necessarily true because most of the data used to calculate the value of 1.04115 had not been normalized to the V-SMOW/SLAP scale. The group consensus was that at present the CO_2-H_2O isotope fractionation factor is not known to five significant figures and there is controversy over the fourth. The degree of uncertainty in this fractionation factor can be illustrated by comparing the value Brenninkmeijer, Kraft, and Mook (1983) determined in their laboratory at 25°C, 1.04111 ± 0.00007, with the value we calculate by normalizing their measurements to the V-SMOW/SLAP scale. We calculate a normalized value of 1.04088 ± 0.00007 using their $\delta^{18}O$ value of SLAP relative to SMOW of -55.76 permil (Table V in Gonfiantini, 1984) and using their $\delta^{18}O$ value of V-SMOW relative to SMOW of -0.05 permil (Gonfiantini, 1984, p. 59). This re-evaluated value differs from theirs by 0.00023, more than far enough to justify elimination of the fifth significant figure in the CO_2-H_2O isotope fractionation factor.



α_1 : $CO_2 \equiv$PDB relative to $CO_2 \equiv$V-SMOW = 1.00027, determined on the normalized V-SMOW/SLAP scale using the defined value of NBS-19 on the PDB scale (Coplen, Kendall, and Hopple, 1983).

α_2 : Taken from Friedman and O'Neil (1977).

α_3 : Defined at the 1983 meeting by adopting a $\delta^{18}O$ value of NBS-19 = -2.20 permil on the PDB scale.

α_4 : $CO_2 \equiv$V-SMOW relative to $CO_2 \equiv$NBS-19 = 1.00193 as measured on the normalized V-SMOW/SLAP scale (Coplen, Kendall, and Hopple, 1983).

α_5 : 1.0309 is the value adopted at this meeting.

α_6 : 1.0415, determined from α_4 and α_5.

Therefore, the conversion equations in units of permil are:

$$\delta^{18}O_{V\text{-}SMOW} = 1.0309\ \delta^{18}O_{PDB} + 30.9$$

$$\delta^{18}O_{V\text{-}SMOW} = 1.0415\ \delta^{18}O_{PDB \equiv CO_2} + 41.5$$

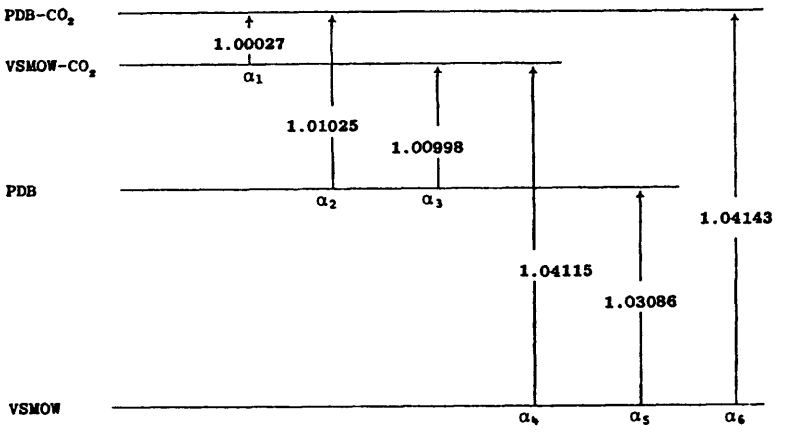
REFERENCES

Coplen, T.B., Kendall, C., and Hopple, J. - 1983: Comparison of stable isotope reference samples. Nature 302, 236-238.

Friedman, I. and O'Neil, J.R. - 1977: Compilation of stable isotope fractionation factors of geochemical interest. U.S. Geological Survey Profess. Paper 440-KK.

Figure 1.--Revised figure 3 of Gonfiantini (1984) showing $\delta^{18}O$ conversion equations [modified from Friedman and O'Neil (1977) and from Gonfiantini (1984)].

Figure 3 - $\delta^{18}O$ CONVERSION EQUATIONS



α_1: α for PDB-CO_2 vs old SMOW-CO_2 = 1.00022 (Craig, 1965), confirmed by Mook (1968). Problem remains whether we define SMOW and V-SMOW to be equal or accept a difference of 0.05 ‰ which according to Mook is realistic.

α_2: Taken from Friedman and O'Neil (1977), see Table XII.

α_4: According to Brenninkmeijer et al. (1983), is the average of 3 independent determinations by 4 different laboratories.

α_5: 1.03086 is exactly the figure quoted by Friedman and O'Neil (1977).

α_6: 1.04143, almost equal to figure by Friedman and O'Neil (+0.01 ‰).

The conversion equations are in general:

$$\delta^{18}O_{lower} = \alpha_i \delta^{18}O_{upper} + (\alpha_i - 1)10^3 \text{ ‰}$$

where $\alpha_i = \alpha_1, \alpha_2, \ldots \alpha_6$, and "lower" and "upper" refer to the standard levels in the scheme.

For instance:

$$\delta^{18}O_{V\text{-}SMOW} = 1.03086\delta^{18}O_{PDB} + 30.86 \text{ ‰}$$

or

$$\delta^{18}O_{V\text{-}SMOW} = 1.04143\delta^{18}O_{PDB\text{-}CO_2} + 41.43 \text{ ‰}$$

References

Craig, H. - 1965: The measurement of oxygen isotope paleotemperatures. Conf. on stable isotopes in oceanographic studies and palaeotemperatures, Pisa, p. 161-182.

Mook, W.G. - 1968: Geochemistry of the stable isotopes of carbon and oxygen in natural waters in the Netherlands. PhD. Thesis, University of Groningen.

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Brnninkmeijer, C.A.M., Kraft, P. and Mook, W.G. - 1983: Oxygen isotope fractionation between CO_2 and H_2O. Isotope Geoscience 1, 181-190.

Figure 2. Figure 3 of Gonfiantini (1984) showing $\delta^{18}O$ conversion equations.

RELATIONSHIP BETWEEN THE SMOW AND PDB SCALES

Gonfiantini (1984, p. 13) presents equations relating the PDB scale to the SMOW scale. For calcite, expressed in permil:

$$\delta_{C\text{-}SMOW} = 1.03086\ \delta_{C\text{-}PDB} + 30.86$$

and for CO_2 samples, expressed in permil:

$$\delta_{G\text{-}SMOW} = 1.04143\ \delta_{G\text{-}CO_2 \equiv PDB} + 41.43$$

where $\delta_{C\text{-}SMOW}$ and $\delta_{C\text{-}PDB}$ are the isotopic abundances of the calcite relative to SMOW and PDB, respectively. Then, $\delta_{G\text{-}SMOW}$ and $\delta_{G\text{-}CO_2 \equiv PDB}$ are, respectively, the δ values of the gas relative to SMOW and relative to CO_2 evolved from PDB calcite at 25°C by 100 percent phosphoric acid. The group consensus was that values of 1.0309 and 30.9 should be used in the first equation above and most conference attendees were vehemently opposed to using numbers with more significant figures, such as 1.03086 and 30.86. The reasoning behind this recommendation is that the CO_2-H_2O isotope fractionation factor, which is the largest fractionation factor used in the determination of this equation, is not known to an accuracy of five significant figures, as discussed above. Therefore, the equation adopted by the group expressed in permil is

$$\delta_{C\text{-}SMOW} = 1.0309\ \delta_{C\text{-}PDB} + 30.9$$

The subsequent equation must also be changed for the same reason and reduces to

$$\delta_{G\text{-}SMOW} = 1.0415\ \delta_{G\text{-}CO_2 \equiv PDB} + 41.5$$

The last equation on page 13 in Gonfiantini (1984) is based solely upon the CO_2-H_2O isotope fractionation factor.

RECOMMENDED $\delta^{18}O$ VALUE OF NBS-19

The IAEA consultants at the 1983 meeting made great progress in tying together the PDB and SMOW oxygen isotope scales by adopting a value of -2.20 permil for NBS-19 calcite relative to PDB calcite. In discussing the

$\delta^{18}O$ value of NBS-19 on the PDB scale, Gonfiantini (1984, p. 14) says, "This value might be modified when more measurements in selected laboratories are available ..." This is contrary to the group consensus. Nearly all of the attendees were delighted that the PDB scale was tied to a calcite reference sample in abundant supply by a firm value that would not be changed. There is no need or desire to modify the value of -2.20 permil.

CONCLUSIONS

Having corrected the equations on page 13 of Gonfiantini (1984), we need to modify figure 3 of Gonfiantini (1984), which is figure 2 herein, to take into account the recommendations of the Advisory Group. These modifications are shown in figure 1. We have added CO_2 evolved from NBS-19 to the figure to take into account the $\delta^{18}O$ value of -2.20 permil of NBS-19 on the PDB scale recommended by the attendees. It is interesting to note that the oxygen isotope fractionation between $CO_2 \equiv$PDB and $CO_2 \equiv$V-SMOW, α_1 in figure 1, determined from α_3 which was defined at this meeting and from α_4 which has been measured on the normalized V-SMOW/SLAP scale, is 1.00027. This is exactly the value in figure 3 of Gonfiantini (1984), figure 2 herein.

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