Calculator of precipitation temperature of sedimentary calcium carbonates based on the oxygen isotope composition (version 11) – notes

The calculator was developed by H. Wierzbowski[1] and is free to use for scientific purposes. A goal of this calculator is to compare precipitation temperatures of calcium carbonate calculated using different oxygen isotope temperature equations, which can be employed in palaeoenvironmental studies. Basically, problems of carbonate oxygen isotope temperatures may arise because of various reference $\delta^{18}O$ values of isotope standards or different calibrations of isotope scales. All appropriate corrections are used in the calculator.

References and notes

Temperatures calculated for calcite:

1. Epstein S., Buchsbaum R., Lowenstam H. A. and Urey, H. C. (1953) Revised carbonate-water isotopic temperature scale. Bulletin of the Geological Society of America 64, 1315–1326. *The equation (1) is established for aragonite-calcitic (predominantly aragonite) mollusc shells in the 7-30°C temperature range. The original $\delta^{18}O$ values of samples studied by Epstein et al. (1953) were decreased by up to 1‰. due to the helium flow roasting. This may have resulted in a change in the original temperature dependence of the $\delta^{18}O$ values of aragonite-calcite mixture and made this equation similar to the temperature dependence of biogenic calcite. For details see: "Wierzbowski H., (2007) Effects of pre-treatments and organic matter on oxygen and carbon isotope analyses of skeletal and inorganic calcium carbonate. Int. J. Mass Spectrom. 268, 16-29". $\delta^{18}O$ values of water and calcium carbonate are reported in the Epstein et al.'s (1953) equation as the values of CO_2 equilibrated with water and the values of acid-liberated CO_2, respectively, and have to be re-calculated for VSMOW and VPDB scales.*

    $$T(°C) = 16.5 - 4.3*(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.14*(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2 \qquad (1)$$

    where $\delta^{18}O_{water}$ are the values of CO_2 equilibrated with water and $\delta^{18}O_{calcite}$ are the values of acid-liberated CO_2

2. Craig H. (1965) The measurement of oxygen isotope paleotemperatures. In: Proceedings of the Spoleto Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures (ed. E. Tongiorgi). Consiglio Nazionale delle Ricerche, Pisa. pp. 161–182. *The author has introduced some instrumental corrections to the original equation of Epstein et al. (1953). $\delta^{18}O$ values of water and calcium carbonate in the equation of Craig (1965) are reported as the values of CO_2 equilibrated with water and the values of acid-liberated CO_2, respectively, and have to be re-calculated for VSMOW and VPDB scales.*

    $$T(°C) = 16.9 - 4.2*(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.13*(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2 \qquad (2)$$

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where $\delta^{18}O_{water}$ are the values of CO_2 equilibrated with water and $\delta^{18}O_{calcite}$ are the values of acid-liberated CO_2

3. Anderson T. F. and Arthur M. A. (1983) Stable isotopes of oxygen and carbon and their application to sedimentologic and paleonvironmental problems. In: *Stable Isotopes in Sedimentary Geology* (eds. M.A. Arthur, T.F. Anderson, I.R. Kaplan, J. Veizer and L. S. Land). SEPM Short Course No.10. pp. 1–151. *The authors have modified the previous equation of Craig (1965) to express $\delta^{18}O$ values of water and calcium carbonate relative to SMOW and PDB scales, respectively. The equation is widely used in palaeoclimatic studies for calcite samples. The equation may additionally be corrected for a new relation established between VSMOW and VPDB scales by Coplen et al. (1983).*

The original Anderson & Arthur's (1983) equation is as follows:

$$T(^oC) = 16.0 - 4.14*(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.13*(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2 \qquad (3)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the PDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the SMOW scale.

4. Friedman I. and O'Neil J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In: Data of Geochemistry, 6th edition. Geochemical Survey Professional Paper 440 – KK. pp. KK1–KK12. *This equation, produced for inorganic calcite for the 0-500°C temperature range, is a corrected version of the equation of O'Neil et al. 1969 (O'Neil. J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys. 51, 5547-5558).*

$$10^3 \ln\alpha_{calcite–water} = 2.78*10^6/T^2 – 2.89 \qquad (4)$$

where $\alpha_{calcite–water}$ is equilibrium fractionation factor between calcite and water, and T is the temperature in Kelvin.

5. Hays, P.D., Grossman, E.L., (1991) Oxygen isotopes in meteoric calcite cements as indicator of continental paleoclimate, Geology 19, 441–444. *The authors have recalculated the equation of Friedman and O'Neil (1977) into a second-order temperature dependence of ($\delta^{18}O_{calcite}$ and $\delta^{18}O_{water}$) values for the 0-60°C temperature range. For the information that the equation is based on formula of Friedman and O'Neil (1997) see: Grossman, E.L., (2012) Oxygen isotope stratigraphy, In: Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M., (Eds). A Geologic Time Scale 2012. Elsevier, pp. 181–206.*

$$T(^oC) = 15.7 - 4.36*(\delta^{18}O_{calcite} - \delta^{18}O_{water}) +0.12*(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2 \qquad (5)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the PDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the SMOW scale.

6. Kim S-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochimica et Cosmochimica Acta 61, 3461–3475. *It is a new temperature equation established for inorganic calcite in the 10-40°C temperature range. As the authors use a new, non-conventional CO_2-calcite acid*

fractionation factor of 1.01050, the equation needs to be re-calculated for an acid fractionation factor of 1.01025 which is conventionally applied for calcite (see also Friedman and O'Neil, 1977; Zhou and Zheng, 2003).

The corrected Kim & O'Neil's (1997) equation is as follows:

$$10^3 \ln\alpha_{calcite-water} = 18.03*10^3/T - 32.17 \qquad (6)$$

where $\alpha_{calcite-water}$ is equilibrium fractionation factor between calcite and water, and T is the temperature in Kelvin.

7. Coplen, T.B., 2007. Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. Geochemica et Cosmochimica Acta 71, 3948–3957. *It is an approximated temperature dependence of oxygen isotope ratio of very slowly naturally precipitated inorganic calcite in the 13-40°C temperature range. The equation gives higher precipitation temperatures than previously constructed oxygen isotope equations for calcite, which is claimed to be a result of maintaining the real oxygen isotope equilibrium for slow-growing calcites.*

$$10^3 \ln\alpha_{calcite-water} = 17.4*10^3/T - 28.6 \qquad (7)$$

where $\alpha_{calcite-water}$ is equilibrium fractionation factor between calcite and water, and T is the temperature in Kelvin.

8. Brand, U, Azmy, K., Bitner, M.A., Logan, A., Zuschin, M., Came, R., Ruggiero, E., 2013. Oxygen isotopes and $MgCO_3$ in brachiopod calcite and a new paleotempeature equation. Chemical Geology 359, 23–31. *It is a new equation for modern calcitic brachiopods covering the temperature range from –2 to +32°C. An adjustment of $\delta^{18}O_{calcite}$ value for shell $MgCO_3$ content (+0.17‰ for 1 mol% of $MgCO_3$) is usually made in this formula according to the data of Jiménez-López et al. (2004). An appropriate adjustment should be calculated for each analyzed clacite sample based on its molar Mg contents.*

$$T(^oC) = 16.192 - 3.468*(\delta^{18}O_{calcite} - \delta^{18}O_{water} - \delta^{18}O_{Mg-adjust.}) \qquad (8)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale, $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale and $\delta^{18}O_{Mg-adjust.}$ is an adjustment for a change of $\delta^{18}O_{calcite}$ for each $MgCO_3$ mol%.

9. Kele, S., Breitenbach, S.F.M., Capezzuoli, E., Meckler, A.N., Ziegler, M., Millan, I.M., Kluge, T., Deák, J., Hanselmann, K., John, C.M., Yan, H., Liu, Z., Bernasconi, S.M., 2015. Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: A study of travertines and tufas in the 6–95 ºC temperature range. Geochemica et Cosmochimica Acta 168, 172–192. *It is a temperature dependence of oxygen isotope ratio of very slowly naturally precipitated calcitis travertines and tufasin the 6-95°C temperature range. The equation gives the highest precipitation temperatures among all presented equations, which is claimed to be a result of approaching the real oxygen isotope equilibrium for slow-growing calcites (and possibly other unknown factors).*

$$10^3 \ln\alpha_{calcite–water} = 16.8*10^3/T – 26 \tag{7}$$

where $\alpha_{calcite–water}$ is equilibrium fractionation factor between calcite and water, and T is the temperature in Kelvin

10. Erez and Luz, (1983) Experimental paleotemperature equation for planktonic foraminifera. Geochimica et Cosmochimica Acta 47, 1025–1031. *It is an equation for cultured calcitic planktonic Globigerinoides sacculifer foraminifers for the 14-30°C temperature range. The authors used a vacuum roasting at 450°C, which might have induced unknown oxygen isotope offset. The equation was criticized by Spero et al. 2003 (Paleoceanography 18, PA000814), who argued that Erez and Luz (1983) did not take into account light conditions and carbonate ion concentrations and that their equation differs from real temperature dependence of $\delta^{18}O_{calcite}$ values of Globigerinoides sacculifer. In addition, the $\delta^{18}O_{water}$ values given in the Erez and Luz's (1983) equation need 0.22‰ conversion to be consistent with the VSMOW scale (cf. Bemis et al. 1998; Grossman, 2012).*

The corrected Erez &Luz's (1983) equation is as follows:

$$T(^oC) = 17 – 4.52*(\delta^{18}O_{calcite}-\delta^{18}O_{water}+0.22) +0.03*(\delta^{18}O_{calcite}-\delta^{18}O_{water}+0.22)^2 \tag{9}$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

11. Bouvier-Soumagnac, Y., Duplessy, J.-C., (1985) Carbon and oxygen isotopic composition of planktonic foraminifera from laboratory culture, plankton tows and recent sediment: implications for the reconstruction of paleoclimatic conditions and of the global carbon cycle. Journal of Foraminiferal Research 15, 302-320. *The authors present two equations for calcitic planktonic foraminifers – Orbulina universa cultured in the 12 hour light/12 hour dark cycles in the laboratory as well as specimens caught using plankton tows from the Indian Ocean. Both equations are calibrated for the 20-30°C temperature range. The $\delta^{18}O_{water}$ values given in the Bouvier-Soumagnac et al.'s (2004) equations need 0.20‰ conversion to be consistent with the VSMOW scale (cf. Bemis et al. 1998).*

The corrected equation for cultured Orbulina universa is as follows:

$$T(^oC) = 16.36 – 4.67*(\delta^{18}O_{calcite}-\delta^{18}O_{water}+0.20) \tag{10A}$$

The corrected equation for Orbulina universa from plankton tows is as follows:

$$T(^oC) = 15.36 – 4.81*(\delta^{18}O_{calcite}-\delta^{18}O_{water}+0.20) \tag{10B}$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

12. Bemis, B.E., Spero, H.J., Bijma, J., Lea, D.W., (1998) Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. Paleoceanography 13, 150–160. *The authors have produced two equations for cultured calcitic planktonic foraminifers – Orbulina*

universa (symbiotic) grown under low and high light intensities between 15 and 25°C and three equations for different size fractions of calcitic Globigerina bulloides (non-symbiotic).

The equation for Orbulina universa – low light is as follows:

$$T(^oC) = 16.5 - 4.8*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (11A)$$

The equation for Orbulina universa – high light is as follows:

$$T(^oC) = 14.9 - 4.8*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (11B)$$

The equation for Globigerina bulloides (non-symbiotic) – 11-chambered shells is as follows:

$$T(^oC) = 12.6 - 5.07*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (11C)$$

The equation for Globigerina bulloides (non-symbiotic) – 12-chambered shells is as follows :

$$T(^oC) = 13.2 - 4.89*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (11D)$$

The equation for Globigerina bulloides (non-symbiotic) – 13-chambered shells is as follows:

$$T(^oC) = 13.6 - 4.77*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (11E)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the PDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the SMOW scale.

13. Lynch-Stieglitz, Curry, W.B., Slowey, N., (1999). A geostrophic transport estimate for the Florida Current from the oxygen isotope composition of benthic foraminifera. Paleoceanography 14, 360-373. *It is an equation for calcitic benthic Cibicidoides-Planulina foraminifera, fitted in the 4-26°C temperature range, based on published data.*

$$T(^oC) = 16.09 - 4.76*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \hspace{3cm} (9)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

14. Mulitza, S., Boltovskoy, D., Donner, B., Meggers, H., Paul, A., Wefer, G., (2003) Temperatur:δ^{18}O relationships of planktonic foraminifera collected from surface waters. Palaeogeography, Palaeoclimatology, Palaeoecology 202, 143-152. *The authors present four oxygen temperature equations for calcitic planktonic foraminifers – Globigerinoides sacculifer, Globigerinoides rubber (white), Globigerina bulloides and Neogloboquadrina pachyderma collected from plankton tows, for temperature ranges of 16° to 32°C, 16° to 32°C, 1° to 26°C and -2° to 14°C, respectively. $\delta^{18}O_{water}$ values given in the Mulitza et al.'s (2003) equation need 0.27‰ conversion to be consistent with the VSMOW scale.*

The Globigerinoides sacculifer equation is as follows:

$$T(^oC) = 14.91 - 4.35*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (13A)$$

The Globigerinoides rubber (white) equation is as follows:

$$T(^oC) = 14.2 - 4.44*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (13B)$$

The Globigerina bulloides equation is as follows:

$$T(^oC) = 14.62 - 4.7*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (13C)$$

The Neogloboquadrina pachyderma equation is as follows:

$$T(^oC) = 12.69 - 3.55*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (13D)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

15. Barras, C., Duplessy, J.-C., Geslin, E., Michel, E., Jorissen, F.J., (2010) Calibration of $\delta^{18}O$ of cultured benthic foraminiferal calcite as a function of temperature. Biogeosciences 7, 1349–1356. *The authors produced four equations for different size fractions of calcitic cultured benthic foraminifers – Bulimina marginata for the 4-19°C temperature range. $\delta^{18}O_{water}$ values given in the Barras et al.'s (2010) equation need 0.27‰ conversion to be consistent with the VSMOW scale.*

The equation for Bulimina marginata foraminifers (≤150 μm size fraction) is as follows:

$$T(^oC) = 15.25 - 4.54*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (14A)$$

The equation for Bulimina marginata foraminifers (150 - 200 μm size fraction) is as follows:

$$T(^oC) = 15.73 - 4.49*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (14B)$$

The equation for Bulimina marginata foraminifers (200 - 250 μm size fraction) is as follows:

$$T(^oC) = 16 - 4.61*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (14C)$$

The equation for Bulimina marginata foraminifers (>250 μm size fraction) is as follows:

$$T(^oC) = 16.93 - 5.31*(\delta^{18}O_{calcite} - \delta^{18}O_{water} + 0.27) \qquad (14D)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

16. <u>Marchitto, T.M., Curry, W.B., Lynch-Stieglitz, J., Bryan, S.P., Cobb, K.M., Lund, D.C., (2014) Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera. Geochimica et Cosmochimica Acta 130, 1–11.</u> *The authors produced two equations for calcitic benthic foraminifers – Cibicidoides-Planulina and Uvigerina based on new and published data, for the temperature range of –0.6 to 25.6°C and 0.8 to 19°C, respectively. In the calculator are used superior quadratic fits of all these equations.*

The Cibicidoides-Planulina equation is as follows:

$T(^oC) = \{0.245 - [0.045461 + (0.0044*(\delta^{18}O_{calcite} - \delta^{18}O_{water})]^{1/2}\}/0.0022$ 　　　　(15A)

The Uvigerina equation is as follows:

$T(^oC) = \{0.242 - [0.046468 + (0.0032*(\delta^{18}O_{calcite} - \delta^{18}O_{water})]^{1/2}\}/0.0016$ 　　　　(15B)

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

Temperatures calculated for aragonite:

1. <u>Grossman E. L. and Ku T-L. (1986) Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. Chemical Geology 59, 59–74.</u> *The authors present two equations "for molluscs" and "for all (skeletal) data" based on measurements of isotopic composition of modern aragonitic molluscs and foraminifers in the 2.6-22.0°C range. Both equations need corrections to the $\delta^{18}O_{water}$ value as the authors report $\delta^{18}O$ values of the water as being lower by 0.2‰ compared to the SMOW scale.*

The original Grossman & Ku's (1986) equation for "all data" is as follows:

$T(^oC) = 20.6 - 4.34*(\delta^{18}O_{aragonite} - \delta^{18}O_{water} + 0.2)$ 　　　　(1A)

The original Grossman & Ku's (1986) equation for "molluscs" is as follows:

$T(^oC) = 21.8 - 4.69*(\delta^{18}O_{aragonite} - \delta^{18}O_{water} + 0.2)$ 　　　　(1A)

where $\delta^{18}O_{aragonite}$ is the oxygen isotope composition of carbonate on the PDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the SMOW scale.

2. <u>Böhm F., Joachimski M. M., Dullo W-C., Eisenhauer A., Lehnart H., Reitner J. and Wörheide G. (2000) Oxygen isotope fractionation in marine aragonite of coralline sponges. Geochimica et Cosmochimica Acta 64, 1695–1703.</u> *The authors present two similar equations, given as fractionation factor formula and a linear temperature dependence of ($\delta^{18}O_{aragonite}$ - $\delta^{18}O_{water}$) values, respectively. The equations are based on published isotope data for aragonitic fossils, synthetic aragonites and new data from coralline sponges for the 3-28°C temperature range.*

The fractionation factor Böhm et al.'s (2000) equation is as follows:

$$10^3 \ln\alpha_{aragonite-water} = 18.45*10^3/T - 32.54 \hspace{4cm} (2A)$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin.

The linear Böhm et al.'s (2000) equation is as follows:

$$T(^oC) = 20.0 - 4.42*(\delta^{18}O_{aragonite} - \delta^{18}O_{water}) \hspace{3cm} (2B)$$

where $\delta^{18}O_{aragonite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

3. <u>Zhou, G-T., Zheng, Y-F., (2003) An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. Geochimica et Cosmochimica Acta 67, 387–399.</u> *It is an equation established for synthetic aragonites in the 0-70°C temperature range. The equation was criticized by Kim et al. 2007 (see the quotation below), who suggested that Zhou et al.'s (2003) is affected by kinetic fractionation effects, which may explain obtained low $\delta^{18}O_{aragonite}$ values (therefore, also evidently low temperatures calculated using this equation).*

$$10^3 \ln\alpha_{aragonite-water} = 20.44*10^3/T - 41.48 \hspace{4cm} (3)$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin.

4. <u>Kim., S-T., O'Neil, J.R., Hillaire-Marcel, C., Mucci, A., (2007) Oxygen isotope fractionation between synthetic aragonite and water. Influence of temperature and Mg^{2+} concentrations. Geochimica et Cosmochimica Acta 71, 4704–4715.</u> *It is a new equation established for inorganic aragonites in the 10-40°C temperature range. As the authors used a new, non-conventional CO_2-aragonite acid fractionation factor of 1.01063 the equation needs to be re-calculated to be consistent with CO_2-calcite acid fractionation factor of 1.01025 which is generally used for measurements of $\delta^{18}O_{aragonite}$ values in many laboratories (see also Friedman and O'Neil; 1977).*

$$10^3 \ln\alpha_{aragonite-water} = 17.88*10^3/T - 30.76 \hspace{4cm} (4)$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin.

5. <u>Patterson W. P., Smith G. R. and Lohmann K. C. (1993) Continental paleothermometry and seasonality using the isotopic composition of aragonite otoliths of freshwater fishes. In: Climate Change in Continental Isotopic Records (eds. P. K. Swart, K. C. Lohmann, J. McKenzie and S. Savin). Geophysical Monograph 78. pp. 191–202.</u> *It is an equation produced by analyses of the isotope composition of otoliths of naturally grown and reared fishes in the 3.2-30.3°C temperature range, given as a fractionation factor formula.*

$$10^3 \ln\alpha_{aragonite-water} = 18.56*10^3/T - 33.49 \hspace{4cm} (5)$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin

6. Thorrold S. R., Campana S. E., Jones C. M. and Swart P. K. (1997) Factors determining $\delta^{13}C$ and $\delta^{18}O$ fractionation in aragonitic otoliths of marine fish. Geochimica et Cosmochimica Acta 61, 2909–2919. *It is an equation produced by analyses of isotope composition of otoliths of reared fishes in the 18.2-25.0°C temperature range.*

$$10^3 \, ln\alpha_{aragonite-water} = 18.56*10^3/T – 32.54 \tag{6}$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin

7. White, R.M.P., Dennis, P.F., Atkinson, T.C., (1999) Experimental calibration and field investigation of the oxygen isotopic fractionation between biogenic aragonite and water. Rapid Communications in Mass Spectrometry 13, 1242–1247. *It is an equation established for freshwater molluscs in the 8-24°C temperature range and given as fractionation factor and linear temperature dependence of ($\delta^{18}O_{aragonite}$ - $\delta^{18}O_{water}$) values.*

The fractionation factor White et al.'s (1999) equation is as follows:

$$10^3 \, ln\alpha_{aragonite-water} = 16.74*10^3/T – 26.39 \tag{7A}$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin

The linear White et al.'s (1999) equation is as follows:

$$T(°C) = 21.36 – 4.83*(\delta^{18}O_{aragonite} – \delta^{18}O_{water}) \tag{7B}$$

where $\delta^{18}O_{aragonite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

8. Høie, H., Otterlei, E., Folkvord, A., 2004. Temperature-dependent fractionation of stable oxygen isotopes in otoliths of juvenile cod (*Gadus morhua* L.). ICES Journal of Marine Sciences 61, 243–251. *It is an equation established for otoliths of reared fishes for the range of 6-20°C, which is given in two forms – as a fractionation factor formula and linear temperature dependence of ($\delta^{18}O_{aragonite}$ - $\delta^{18}O_{water}$) values. The latter equation need 0.22‰ conversion to be consistent with the VSMOW scale (cf. Høie et al. 2004).*

The fractionation factor Høie et al.'s (2004) equation is as follows:

$$10^3 \, ln\alpha_{aragonite-water} = 16.75*10^3/T – 27.09 \tag{8A}$$

where $\alpha_{aragonite-water}$ is equilibrium fractionation factor between aragonite and water, and T is the temperature in Kelvin

The linear Høie et al.'s (2004) equation is as follows:

$$T(^oC) = 21.36 - 4.83*(\delta^{18}O_{aragonite} - \delta^{18}O_{water} + 0.22) \qquad (8B)$$

where $\delta^{18}O_{aragonite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

9. <u>Marchitto, T.M., Curry, W.B., Lynch-Stieglitz, J., Bryan, S.P., Cobb, K.M., Lund, D.C., (2014) Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera. Geochimica et Cosmochimica Acta 130, 1–11.</u> *The authors present equations for aragonitic benthic foraminifers – Hoeglundina elegans and Uvigerina equation, based on new and published data, which are calibrated for the 10.8-19°C temperature range. In the calculator are used superior quadratic fits of these equations.*

The Hoeglundina elegans equation is as follows:

$$T(^oC) = \{0.243 - [0.0536611 + (0.0012*(\delta^{18}O_{calcite} - \delta^{18}O_{water})]^{1/2}\}/0.0006 \qquad (9)$$

The Uvigerina equation is as follows:

$$T(^oC) = \{0.242 - [0.046468 + (0.0032*(\delta^{18}O_{calcite} - \delta^{18}O_{water})]^{1/2}\}/0.0016 \qquad (15B)$$

where $\delta^{18}O_{calcite}$ is the oxygen isotope composition of carbonate on the VPDB scale and $\delta^{18}O_{water}$ is the oxygen isotope composition of water on the VSMOW scale.

For (V)PDB – (V)SMOW conversions see:

1. Coplen, T.B., Kendall, C., Hopple, J. (1983) Comparison of stable isotope reference samples. *Nature* 302, 236–238.
2. Friedman I. and O'Neil J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In: *Data of Geochemistry, 6th edition.* Geochemical Survey Professional Paper 440 – KK. pp. KK1–KK12.

For fractionation factor between CO_2 derived from acid decomposition of (V)PDB and (V)PDB as well as fractionation factor between CO_2 equilibrated with (V)SMOW and (V)SMOW see:

1. Friedman I. and O'Neil J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In: *Data of Geochemistry, 6th edition.* Geochemical Survey Professional Paper 440 – KK. pp. KK1–KK12.
2. Hut, G. (1987) Consultants' Group Meeting on stable isotope reference samples for geochemical and hydrological investigations, IAEA, Vienna, 16-18 September 1985. *Report to the Director General, IAEA, Vienna*, 1-42.