

# $\delta^{13}\text{C}$ in low temperature, $\text{CO}_2$ -charged waters: a need for consistency with carbonate chemistry

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## Introduction

Much data on carbon isotopes in  $\text{CO}_2$ -charged waters have been published. However, the procedure applied for the interpretation of carbon isotope measurements is frequently the same as in typical groundwaters with low  $P_{\text{CO}_2}$  pressures ( $\sim 10^{-3}$  MPa). The obtained  $\delta^{13}\text{TDC}$  values are interpreted in terms of  $\delta^{13}\text{HCO}_3^-$ , which is inconsistent with the carbonate chemistry based on pH and alkalinity measurements made in-situ. Therefore, some examples are critically evaluated and a correct interpretation of the isotopic data is given.

## Discussion

When waters containing  $\text{CO}_2$  gases rise to the surface the loss of hydrostatic pressure enables the separation of a  $\text{CO}_2$  gas phase. Measurements of  $\delta^{13}\text{C}$  of total dissolved carbonates (TDC) and/or  $\delta^{13}\text{C}$  of the gas itself are used to characterise the carbonate system of interest. These two measurements, if interpreted properly completely define the carbonate system. Therefore, if  $\delta^{13}\text{TDC}$ ,  $\delta^{13}\text{CO}_2(\text{g})$  and pH are measured and chemical analyses made at the outflow, it is possible to calculate  $\delta^{13}\text{HCO}_3^-$ .  $\delta^{13}\text{HCO}_3^-$  can also be calculated from  $\delta^{13}\text{CO}_2(\text{g})$  and a known fractionation factor between  $\text{CO}_2$  gas and bicarbonate. If we assume emergence temperature as the temperature of the last equilibration,  $\delta^{13}\text{HCO}_3^-$  calculated in this way can be compared with  $\delta^{13}\text{HCO}_3^-$  calculated from the measurement of  $\delta^{13}\text{TDC}$  and carbonate species distributions. Therefore, the isotopic equilibrium between bicarbonate and  $\text{CO}_2$  gas can be verified.

In several works concerned with  $\text{CO}_2$ -charged waters there is the wrong assumption that the carbon isotopic composition of the precipitated in the field carbonates ( $\text{BaCO}_3$  or  $\text{SrCO}_3$ ) is equivalent to the isotopic composition of  $\text{HCO}_3^-$ . However, in several cases of low carbonated, low pH waters charged with  $\text{CO}_2$  gas,  $\text{CO}_2(\text{aq})$  concentration is higher than  $\text{HCO}_3^-$ . During precipitation,  $\delta^{13}\text{C}$  value is frozen and when measured as  $\delta^{13}\text{TDC}$ , it reflects the contribution

of particular carbonate species to the TDC, i.e.  $\text{CO}_2(\text{aq})$  and  $\text{HCO}_3^-$ . However, the presence of  $\text{CO}_2(\text{aq})$  is not fully appreciated. For example, Shotterer *et al.* (1989) suggested that  $\text{CO}_2(\text{g})$  is not in equilibrium with dissolved bicarbonate in  $\text{CO}_2$ -rich waters in the Engadine Valley, Switzerland. Though their measured  $\delta^{13}\text{C}$  values of carbonate precipitates concern total dissolved carbonate, they interpreted the results as if  $\delta^{13}\text{C}$  were of  $\text{HCO}_3^-$ . Based on the chemical analyses reported by Wexsteen *et al.* (1988),  $\text{HCO}_3^-$  contributes to the TDC in the  $\text{CO}_2$ -rich springs of the Engadine Valley by less than 50%: 45% in Lucius, 36% in Sfondraz, 42% in Bonifacius, 42% Emerita, the other contributing species being  $\text{CO}_2(\text{aq})$ . As a result  $\delta^{13}\text{C}$  of bicarbonate itself (i.e. TDC less  $\text{CO}_2(\text{aq})$ ) must be about 5 per mille instead of reported values around zero per mille. With a gas  $\delta^{13}\text{C}$  average value of about -5 per mille (Shotterer *et al.*, 1989) the system is close to isotopic equilibrium if the fractionation factor of Mook *et al.* (1974) of about 1.010 between bicarbonate and  $\text{CO}_2$  gas is considered at the reported temperatures. Therefore, the conclusion about isotopic disequilibrium between  $\text{CO}_2(\text{aq})$  and dissolved carbonate species could not apply to the springs of the Engadine Valley.

Though  $\delta^{13}\text{CO}_2(\text{g})$  values are measured in the hope that these are samples of deep  $\text{CO}_2(\text{g})$ , due to fractionation processes, isotopic composition of the exsolved  $\text{CO}_2$  should be different to that of the source region. In view of the above, it is surprising that  $\delta^{13}\text{CO}_2(\text{g})$  values are similar to those expected for  $\delta^{13}\text{CO}_2(\text{g})$  of deep  $\text{CO}_2$ . This is partly because fractionation during outgassing is not large and accumulated and/or isolated  $\text{CO}_2$  have similar  $\delta^{13}\text{C}$  values. If gas-solution isotopic equilibrium is verified, by additional data on water/gas ratios it is theoretically possible to evaluate  $\delta^{13}\text{C}$  of the carbon source. With the equations for total carbon mass and isotopic balances:  $\text{TC} = \text{CO}_2(\text{g}) + \text{TDC}$  and  $\delta^{13}\text{TC} = X_{\text{CO}_2(\text{g})}\delta^{13}\text{CO}_2(\text{g}) + X_{\text{TDC}}\delta^{13}\text{TDC}$  we have two unknowns in two equations, i.e. TC and  $\delta^{13}\text{TC}$ .  $X$  designates contribution of particular species to the TDC.

Matthews *et al.* (1987) incorrectly assumed that the total carbon inventory consisted of free  $\text{CO}_2$

gas and dissolved  $\text{HCO}_3^-$  (pp.124). They used  $\delta^{13}\text{TDC}$  as if it were  $\delta^{13}\text{HCO}_3^-$ . If the presence of  $\text{CO}_2(\text{aq})$  is considered, then for the Chassol borehole (the Massif Central of France) with  $\delta^{13}\text{TDC}$  claimed to be  $^{13}\text{HCO}_3^- = 1.12$ ,  $\delta^{13}\text{CO}_2(\text{g}) = -5$  per mille and the molar  $\text{HCO}_3^-/\text{CO}_2(\text{g})$  equal to 0.4 as given, the value of true  $\delta^{13}\text{HCO}_3^-$  would be higher. Consequently,  $\delta^{13}$  of the total carbon inventory would also be higher. Similarly, using the data of Griesshaber *et al.* (1992) and the fractionation factor of Mook *et al.* (1974), I calculated the results for  $\text{CO}_2$ -rich water in Lahnstein in the Rhenish Massif. True  $\delta^{13}\text{HCO}_3^-$  is about +2.5 per mille instead of -0.98 claimed to be the measured  $\delta^{13}\text{HCO}_3^-$ . Therefore the total carbon inventory is -2.5 per mille instead of -3.23 per mille.

Another not appreciated problem though addressed earlier (Pearson *et al.*, 1979; Lesniak, 1985), is that during ascent and outgassing  $\delta^{13}\text{TDC}$  depends on  $P_{\text{CO}_2}$ , therefore, the reported  $\delta^{13}\text{TDC}$  is interpretable only if  $P_{\text{CO}_2}$  is reported. Thus, some reference pressure and temperature should be given in addition to  $\delta^{13}\text{TDC}$  measurements.

### Summary

It was found frequently that in  $\text{CO}_2$ -rich waters measurements of  $\delta^{13}\text{TDC}$  are inconsistent with carbonate chemistry and  $\delta^{13}\text{TDC}$  is mistakenly

considered as  $\delta^{13}\text{HCO}_3^-$ . Because  $\delta^{13}\text{TDC}$  values are  $P_{\text{CO}_2}$  dependent, it is proposed that all  $\delta^{13}\text{TDC}$  measurements in  $\text{CO}_2$ -rich waters below boiling point are to be made with reference to f. example 0.1MPa of  $P_{\text{CO}_2}$  and 25 degrees centigrade.  $P_{\text{CO}_2}$  may be calculated from pH and alkalinity measurements or measured directly.  $\delta^{13}\text{TDC}$  at the reference pressure may be recalculated using Raleigh equations in the form presented by Wigley *et al.* (1978).

### References

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