

**Schweitenkirchen, June 2014**

## **Sulphur ( $^{34}\text{S}$ )**

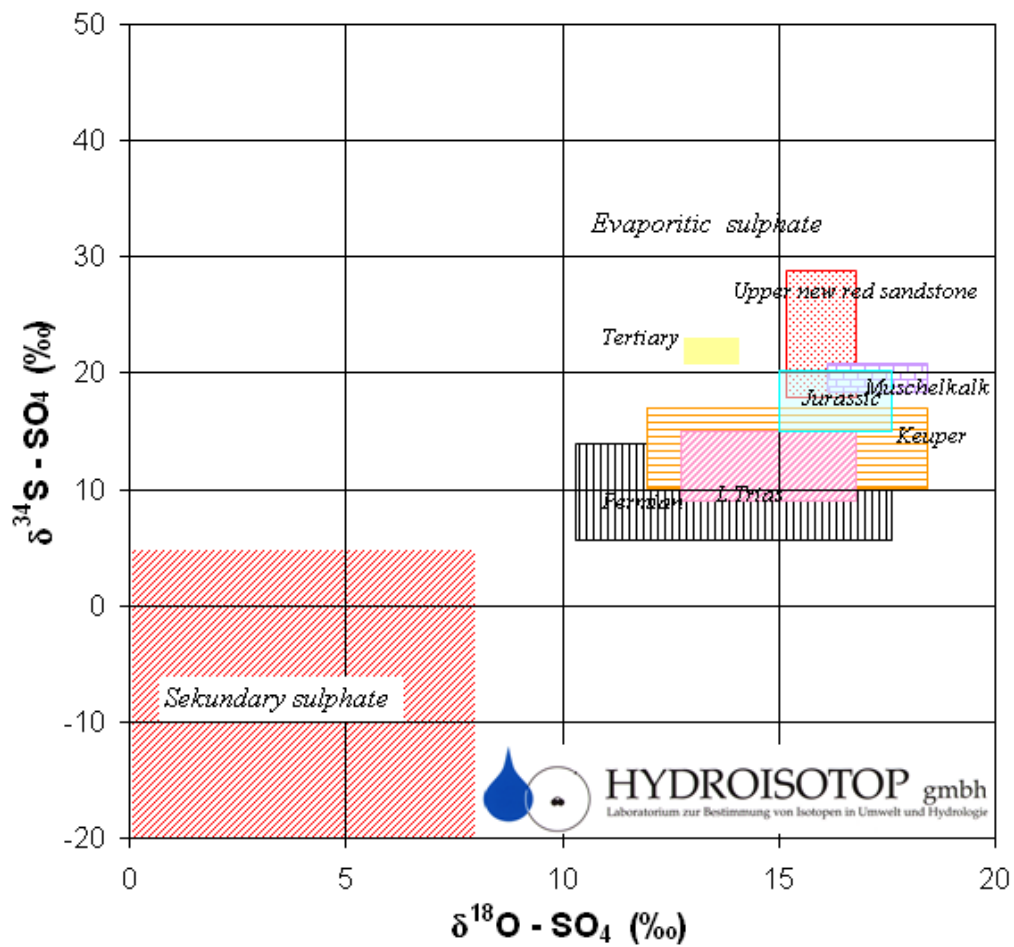
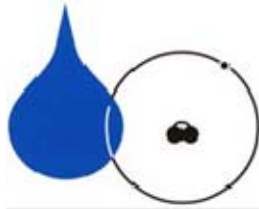
Sulphur has naturally occurring four stable isotopes, namely  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$ .  $^{32}\text{S}$  represents the most abundant isotope with 95.02 %.  $^{34}\text{S}$  is with its amount of 4.21 % the second most abundant sulphur isotope. All further isotopes only occur in nominal abundances and thus only play a minor role for environmental analytics.

Isotope contents of  $^{34}\text{S}$  are considered in relation to  $^{32}\text{S}$  ( $^{34}\text{S}/^{32}\text{S}$ ). This isotope ratio is related to a standard (VCDT – „Vienna Canyon Diablo Troilite“) and specified in the delta notation. Due to small values, it is given in per mille (‰-VCDT).

One of the key factors of sulphur input in ecosystems is the release of sulphur when burning fossil fuels as they contain up to 4 % sulphur. Further on, inputs of sulphur occur by oxidation of sulfur compounds, by release from oceans and inundated soils, as well as subsidiary by volcanic activities.

For hydrological questions, sulphur isotope ratios are mainly measured on sulfate ( $\text{SO}_4$ ). By the combined measurement of sulphur ( $^{34}\text{S}$ ) and oxygen ( $^{18}\text{O}$ ), the origin of sulfate and mixing processes can be identified. Hence, organically bound sulphur and sulfide (Pyrite, Zinc Blende) typically have low  $\delta^{34}\text{S}$  values, whereas inorganic sulfate ( $\text{CaSO}_4$ ,  $\text{SO}_2$ ), especially from evaporates, show more positive values. In addition, microbial activities in groundwater, so called secondary processes such as pyrite oxidation and sulphate reduction, can be verified. To do so,  $^{34}\text{S}$  and  $^{18}\text{O}$  of sulfate and sulphur isotopes of sulfidic compounds (e.g.  $\text{H}_2\text{S}$ ,  $\text{S}^{2-}$ ,  $\text{HS}^-$ ) are analyzed combined. Then, the secondarily produced sulfate and geogen produced sulfate can be differentiated distinctly by its values (Figure 1).

Sulfate isotopes are measured by “Isotope Ratio Mass Spectrometry“ (IRMS), after conversion into  $\text{SO}_2$  and  $\text{CO}$ , respectively.



**Fig. 1:** Data ranges of  $^{34}\text{S}$  and  $^{18}\text{O}$  from sulphate together with the development directions during reduction and oxidation.