

## Geochemical trends in rutile forming reactions

G. L. LUVIZOTTO AND T. ZACK

Mineralogisches Institut, Universität Heidelberg, Germany  
(gluvizot@min.uni-heidelberg.de;  
tzack@min.uni-heidelberg.de)

We are investigating the behavior of trace elements in prograde rutile growth reactions. Our aim is to understand how trace elements are behaving during metamorphic reactions, giving special attention to accessory minerals.

One rutile-forming reaction is observed in low- to medium grade (480°C / 0.6-0.9GPa) metapelitic rocks (Ms+Chl+Qtz+Ilm+Rt+Gra+Ap+Zrn+Mz; in order of abundance) from the Garnet-Phyllite Unit of the Erzgebirge (Germany), where rutile starts to crystallize from Ilm according to the simplified reaction:  $\text{Ilm} + \text{Silicate} + \text{H}_2\text{O} \leftrightarrow \text{Rt} + \text{Chl}$ .

The other reaction, observed in the rocks from the Ivrea Zone (northern Italy), takes place in the transition between amphibolite and granulite facies, where rutile-free amphibolite facies (620°C, 0.4GPa) metapelites (Qtz+High-Ti Bt+Sil+Pl+Grt±Ms) are replaced, with increasing metamorphic grade, by rutile-bearing granulite facies (820°C, 0.8GPa) restitic rocks (Grt+Sil+Qtz+Pl+Kfs±High-Ti Bt). The rutile formation is associated with high-Ti Bt breakdown and is coupled to melting reactions such as  $\text{Bt} + \text{Sil} \rightarrow \text{Grt} + \text{Kfs} + \text{melt}$ .

Remarkably in the two areas, both the rutile-free precursor rock and the rutile-bearing "final product" are present, allowing comparison of the rutile trace element geochemistry in different stages of the reaction. In both cases, during the early stage of rutile formation, its Nb/Ti ratio is strongly controlled by the ratio of the precursor mineral (Ilm and Bt), being evidenced by a large inter-grain spread and Nb/Ti ratios different from those expected for rutiles occurring in equilibrium with the mineral assemblage in question. These features reflect the trace element partitioning between the minerals involved in the reaction and are in good agreement with the published partition coefficient between Ilm[1], Bt[2], Rt[3] and melt. In both examples, as the reactions evolve with increasing metamorphic conditions, the rutile Nb/Ti ratios change toward the value expected for a rutile occurring in equilibrium with the paragenesis in question. Furthermore, in order to equilibrate the rutile Nb/Ti ratio, Nb has to be mobilized, at least on a thin section scale.

### References

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## Excess $^{17}\text{O}$ – A new tracer in hydrology

BOAZ LUZ AND EUGENI BARKAN

The Institute of Earth Sciences, Hebrew University, Jerusalem 91904, Israel (boaz.luz@huji.ac.il)

For more than four decades, water isotope ratios ( $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ ) have played a key role in understanding the hydrologic cycle. For lack of analytical precision, it has been assumed that the  $^{17}\text{O}/^{16}\text{O}$  ratio does not significantly deviate from a constant relation to  $^{18}\text{O}/^{16}\text{O}$  and its measurement seemed redundant. Here we show that when all oxygen isotope ratios are measured with very high precision, they yield a wealth of valuable information.

We have designed and constructed an automatic fluorination system for producing pure  $\text{O}_2$  from water samples. This allows isotope ratio measurements by dual inlet mass spectrometry with overall duplicate difference better than 0.06 ‰ for  $\delta^{18}\text{O}$ . The analytical errors in  $\delta^{17}\text{O}$  are mass dependent on the  $\delta^{18}\text{O}$  errors and therefore are less than 0.03 ‰. This allows determination of the relationships between  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  with extremely high precision.

Using this method together with experimental setups we determined the exponent ( $\theta$ ;  $^{17}\alpha = ^{18}\alpha^\theta$ ) relating the fractionation factors in vapor-liquid equilibrium and vapor diffusion in air as  $0.529 \pm 0.001$  and  $0.519 \pm 0.0006$  respectively. The exponents do not depend on temperature. We also determined the global slope  $\ln(\delta^{17}\text{O} + 1) / \ln(\delta^{18}\text{O} + 1)$  for meteoric water as  $0.528 \pm 0.001$ .

Our measurements show that meteoric water and atmospheric moisture samples fall above a line with a slope 0.528 that originates from VSMOW and thus have an excess of  $^{17}\text{O}$  with respect to seawater. This excess is defined as:

$$^{17}\text{O-excess} = \ln(\delta^{17}\text{O} + 1) - 0.528 \ln(\delta^{18}\text{O} + 1)$$

The precision in measurements of the  $^{17}\text{O-excess}$  is 8 per meg (per meg = 0.001 ‰).

The magnitude of  $^{17}\text{O-excess}$  of meteoric water and atmospheric moisture is in the range of 10 to 70 per meg. It originates, similarly to deuterium excess, from evaporation that is affected by both isotope equilibrium and diffusion transport in air. Yet, in contrast to deuterium excess,  $^{17}\text{O-excess}$  is independent of temperature in liquid-vapor equilibrium and, therefore, it is a simpler indicator of hydrologic processes.

In general,  $^{17}\text{O-excess}$  in precipitation increases when the source vapor is derived from a region where there is large humidity contrast between the ocean surface and the overlying atmosphere. In contrast, its magnitude decreases in evaporating water bodies as well as in leaf water at low humidity. This behavior will be demonstrated in examples from meteoric waters and polar ice.

### References

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