

Fluorite (U-Th)/He thermochronology

R. WOLFF^{1*}, I. DUNKL², H.V. EYNATTEN³

¹University of Göttingen, GZG-Sedimentology, Göttingen, Germany, rwofff@gwdg.de

²University of Göttingen, GZG-Sedimentology, Göttingen, Germany, idunkl@gwdg.de

³University of Göttingen, GZG-Sedimentology, Göttingen, Germany, heynatt@gwdg.de

Why fluorite?

The (U-Th)/He method is a low-temperature thermochronometer dating single crystals. It uses the ⁴He accumulation from the radioactive decay of U, Th and Sm. The most used U and Th bearing accessory minerals are apatite and zircon with closure temperatures of 60 - 70 and ~180 °C. However, more minerals are suited for (U-Th)/He chronology. Fluorite is one of these because it is quite common all over the world, occurs in high- and low-temperature felsic hosted hydrothermal veins and Mississippi Valley Type (MVT) ore deposits. Moreover, its geochemistry is well studied. Consequently, fluorite (U-Th)/He chronology is promising for dating hydrothermal events, secondary fluorite formation in limestones, or regional cooling events.

First results indicate the potential of this method [1,2,3,4,5]. However, the reported diffusion parameters and closure temperatures differ greatly. According to [3] the parameters are $E_a = 30.5 \pm 3.9$ kcal/mol, $\log(D_0/r^2) = 4.9 \pm 0.6$ s⁻¹ and $T_c = 90 \pm 10$ °C (10°C/Ma, 1 - 3 mm) but [4] reports a closure temperature of $T_c = 200$ °C. Thus we decided to follow a two-fold strategy.

Approach and Results

On the one hand we perform a regional study in the Erzgebirge, Germany, that combines analysis of fluorite with the thermal history of the study area constrained by well established thermochronometers. The comparison of the results will indicate the closure temperature of fluorites for this case study. Diffusion experiments on the other hand give laboratory based information on the closure temperature and the diffusion parameters.

Our fluorite (U-Th)/He data fit well into the independently measured Upper Cretaceous to Paleocene regional cooling history of the Erzgebirge and the diffusion experiments suggest a behaviour of fluorite similar to Durango apatite.

Conclusions and Outlook

The results show that fluorite is suitable for low-temperature thermochronology. This opens a window into the chronology of hydrothermal systems, limestones and MVT ore deposits. Additional attention has to be turned on fluorite because it occurs in a variety of colors (colorless, yellow, pink, brown, green, blue, black, fetid fluorite). Due to changes in chemistry and REE patterns they may show also changes in diffusion kinetics.

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Calcite growth kinetics and solution stoichiometry

M. WOLTERS^{1,2*}, G. NEHRKE³, P. VAN CAPPELLEN⁴

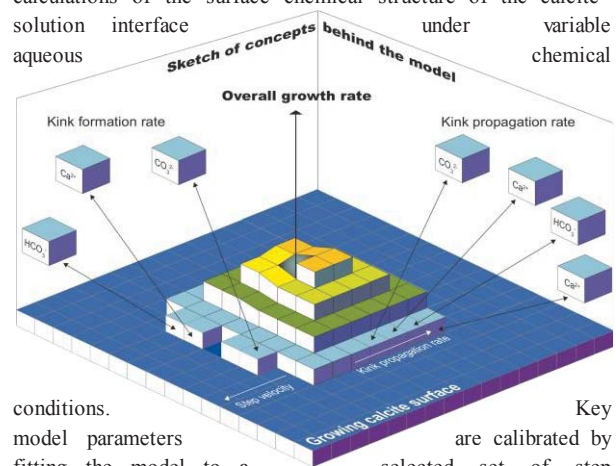
¹Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands, m.wolthers@uu.nl (* presenting author)

²Department of Chemistry, University College London, London, United Kingdom.

³Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany, Gernot.Nehrke@awi.de

⁴Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada, pvc@uwaterloo.ca

The influence of solution stoichiometry on calcite crystal growth kinetics has recently attracted increasing attention. Here we present a process-based calcite growth model (Figure, adapted from [1]) that is founded in a surface structural model for the calcite–aqueous solution interface [2] and extends the growth model for binary symmetrical electrolyte crystals [3]. The model combines kinetic descriptions of the incorporation of calcium, carbonate and bicarbonate ions at kink sites along step edges, with equilibrium calculations of the surface chemical structure of the calcite–solution interface under variable chemical



conditions. Key model parameters are calibrated by fitting the model to a selected set of step velocities on calcite surfaces measured by Atomic Force Microscopy [4-5]. Without any further adjustment of the parameter values, the model reproduces the observed dependence of the macroscopic growth rate of single calcite crystals on the solution activity ratio of calcium and carbonate ions under alkaline conditions. A variable surface roughness factor is introduced in order to reconcile the new process-based growth model with bulk precipitation rates measured in seeded calcite growth experiments. For practical applications, we further present empirical parabolic rate equations fitted to bulk growth rates of calcite in common background electrolytes and in artificial seawater-type solutions. Both the process-based and empirical growth rate equations agree with measured calcite growth rates over broad ranges of ionic strength, pH, solution stoichiometry and degree of supersaturation.

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