

## Water Rock Interaction [WRI 14]

# Geochemistry of calcite veins: records of fluid mixing and fluid-rock interaction

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### Abstract

Detailed geochemical investigations of calcite veins, genetically related to intrusions and vein-hosting bedrock, have been used to indicate fluid evolution during intrusion-related hydrothermal mineralization, involving fluid mixing and water rock interaction. The area of investigation is located in the southeast of Sweden. The 1.85 Ga granitoid country rocks and the 0.9 Ga dolerite vein-related intrusions differ in chemical, geochemical, and stable isotope composition. The variation in rare earth and stable isotope composition across calcite veins and the presence of two groups of fluid inclusions suggests mixing of two types of fluids. Light rare earth enrichment and increasing  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios suggest water rock interaction of one/both fluids.

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*Key words:* calcite veins, rare earth elements,  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios and fluid inclusions

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### 1. Introduction

Influence of fluid-rock interaction on rare earth element (REE) behavior in paleo-hydrothermal systems is not fully constrained, and the REE have both been considered as mobile [1] and immobile [2] elements. Understanding of their behavior requires detailed investigation of minerals precipitated from hydrothermal fluids, consideration of country rock composition and initial fluid composition(s). The latter could be estimated from magmatic intrusions genetically related to hydrothermal mineralization.

The aim of this study is to understand behavior of rare earth elements in hydrothermal system by means of detailed investigation of calcite vein composition, vein-related intrusions and country rocks with help of Sr isotope signatures and fluid inclusions.

Calcite veins that were precipitated in fracture network of felsic rocks and are related to mafic intrusions provide an excellent material for assessment of REE mobility and transport in paleo hydrothermal systems. The pool of REE in mono-mineral veins is hosted only by calcite and reflects the composition of fluids from which it was formed. Variation of REE composition across the veins reflects

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the intensity of fluid-rock interaction, although the source of rare earth elements may be traced only if bedrock and initial intrusions have considerably different REE compositions.

Strontium isotopes provide additional tracers of water-rock interaction. Calcite hardly incorporates Rb, and therefore  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios remain constant over time and reflect  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of fluids which calcite precipitated from. In case of variation in the Sr isotope composition between intruding magma and country rock, the variation in  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios will be reflected also in calcite.

## 2. Geological setting

The granitic bedrock at Laxemar, SE Sweden, hosts calcite veins in close relationship to dolerites dykes. These veins originated during the post-magmatic hydrothermal event [3] that occurred after emplacement of 0.9Ga Blekinge-Dalarna dolerite dyke complex. The dolerite complex was formed due to extension-related mafic magmatism [4], within the 1.80Ga bedrock of granites to quartz monzodiorites (and subordinated by fine-grained granites) belonging to Trans-Scandinavian Igneous Belt (TIB) [5].

## 3. Materials and methods

Samples were collected from two drill cores at depths of 50-420 m below the current sea level. This includes three dolerite dykes and five related calcite veins. Each of these veins was investigated in thick section with scanning electron microscope (SEM) and a number of growth zones were selected for further analyses. Geochemical data includes rare earth element composition of each zone and stable isotope analyses ( $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios). Moreover, fluid inclusions were analyzed from each vein specimen from as many growth zones as it was possible. Dolerite dykes were analyzed for bulk chemistry.

SEM analysis was carried out on a Hitachi S-3400N SEM equipped with EDS system. Mass spectrometry analyses of strontium isotopes were performed with a Finnigan MAT 262. The  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios were calibrated using the NBS-987 standard (measured  $0.710260 \pm 0.000012$ ). Accuracy was between  $\pm 0.000005$  and  $\pm 0.000012$  at  $2\sigma$ . Trace element analyses of calcite were performed with laser ablation inductively coupled mass spectrometry (LA-ICP-MS, using Cetax LSX-200 Nd-YAG UV laser system and Agilent 7500 ICP-MS). As a calibration standard a NIST-612 glass was used and  $^{44}\text{Ca}$  as internal standard. The precision was better than 7% and the accuracy was better than 10%. Detection limits for series of lanthanoids were 0.2-5 ppm. Fluid inclusion analyses were carried out on Linkam THM 600 stage with working range is from  $-196^\circ$  to  $-600^\circ\text{C}$ , mounted on a Nikon microscope. Reference materials were synthetic and well-defined fluid inclusions in SynFlinC and in Alpine quartz, respectively. The reproducibility was  $\pm 0.1^\circ\text{C}$  ( $\pm 0.5^\circ\text{C}$  for temperatures below and above  $40^\circ\text{C}$ ). Bulk chemical composition of dolerite dykes were determined by ICP-MS (Perkin Elmer Sciex ELAN 6000, 6100 or 9000 at Actlabs, Canada) following fusing of each sample with lithium metaborate/tetraborate. The blanks and standards were analyzed along with samples.

## 4. Results and discussion

Calcite fillings precipitated in a short time span in at least two hydrothermal episodes, resulting in precipitation of two calcite generations. Generation 1 is present as calcite breccia (Fig.1a) and on the edges (Fig.1c) of the vein if the vein has been reactivated. The youngest generation of calcite either cut calcite breccia (Fig.1a) or occurs in between calcites of the oldest generation (Fig.1c). In the last case, the fracture was reopened almost in the middle and refilled with calcite of younger generation. When precipitation occurred on one occasion, it is difficult to distinguish the generations (Fig.1b)

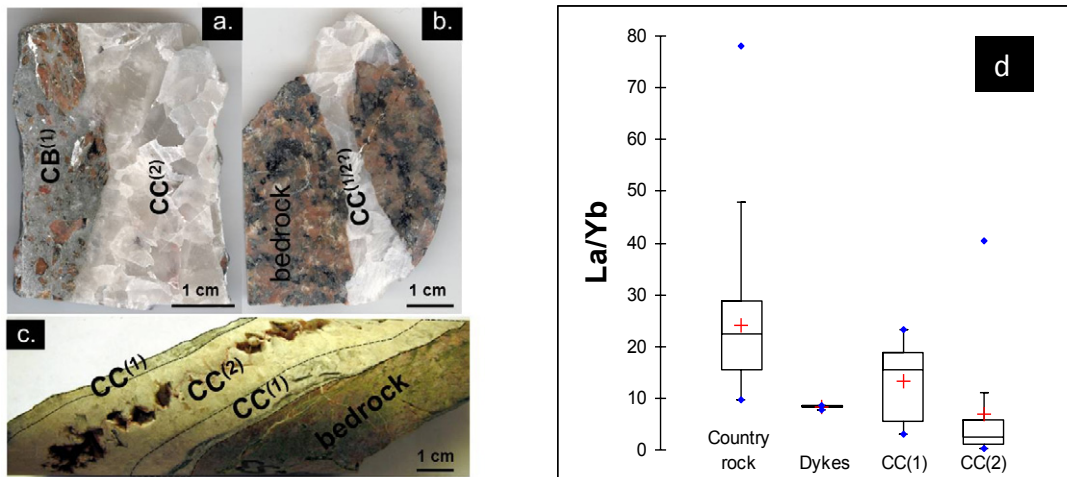


Fig.1 Photos of calcite veins in thick sections (a, b) and in borehole core (c), where CC(1) and CB(1) are calcite veins and calcite breccia of old generation, respectively, and CC(2)-calcite veins of the youngest generation. (d) Box-and-whisker plots of La/Yb-ratios for country rocks, dykes, CC(1) and CC(2). TIB-rock data (country rock) and one dolerite (dykes) analysis are from [6], the rest of the dolerite samples were analyzed in the current study. The box represents the interquartile range. The lower and upper edges of the plot are the first and the third quartiles, respectively. Lines extended outwards of boxes are whiskers. The line across the box indicates the median, cross is the average and dots are max/minim values.

Fluid inclusion measurements show no systematic variation of temperature or salinity between either the two calcite generations or among growth zones in veins. However, the existence of two groups of inclusions: a) low-saline (<10 wt.%  $\text{CaCl}_2$ ) high-temperature ( $\sim T_h=110-126^\circ\text{C}$ ) and b) high-saline ( $\sim 13-24.3$  wt.%  $\text{CaCl}_2$ ) lower-temperature (commonly  $<T_h=110^\circ\text{C}$ ), suggests mixing of two types of fluids, namely relatively warm hydrothermal fluids and cooler brines. Brines may have evolved at great depth from both descended waters from overlying sediments and due to prolonged water-rock interaction with the wall rocks.

Calcite shows significant variation in La/Yb ratios (Fig.1d). LREE enrichment is observed in the oldest generation (median La/Yb=15.5) and is highest for calcite-breccia (median La/Yb=20.7). Calcite of the younger generation is relatively depleted with LREE (median La/Yb=2.39). Comparing dolerite dykes with country rocks, the latter show relative LREE enrichment (Fig.1d). Higher content of LREE in the earlier formed calcite generation could be due to one or a combination of two processes. A large pool of LREE may have been contributed to the calcite-precipitating fluids either from the brines, which have become LREE-enriched due to prolonged low-temperature interaction with country rocks, or from hydrothermal fluids that interacted with fresh bedrock under higher temperature but for a shorter time span. Presence of country rock fragments within calcite-breccia could also increase leaching from TIB-rocks and, consequently, increase the LREE content in the fluid. Lower relative LREE content in the younger generation is either due to less interaction of fluids with country rocks since most of the fracture surfaces were covered by early formed calcite, or due to lower contribution of brines into calcite-originated fluids.

Calcite veins show a wide range of  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios (0.7117-0.7157). Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of dykes and TIB-rocks are  $\sim 0.7046$  [7] and  $\sim 0.7040-0.7081$  [8], respectively. By the time of dykes intrusion, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the TIB-rocks had increased since their emplacement due to decay of Rb and therefore increase of  $^{87}\text{Sr}$ . Increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of TIB-rocks is also confirmed by increasing

$^{87}\text{Sr}/^{86}\text{Sr}$ -ratios of calcite of different generations that were formed from over a long time span [9]. Hydrothermal fluids had similar  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios as dykes, while brine fluids present at that time in fracture network had inherited Sr isotopic composition of TIB-rocks due to a long period of water-rock interaction. Variation in  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios in calcite is a result of mixing of hydrothermal dyke-related fluids and brines, where low  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios reflect dolerite-related source and high  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios reflect brine and/or water-rock interaction with granites of hydrothermal fluids.

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