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# Empirical calibration of the oxygen isotope fractionation between quartz and Fe–Mg-chlorite

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## Abstract

An empirical calibration has been made of the oxygen isotope fractionation between chlorite and quartz, using samples from localities in metamorphic terrains where the formation temperature has been constrained by independent methods (e.g., fluid inclusion homogenization temperatures, mineral assemblages and petrology of the host rocks to the veins, thermodynamic modeling, and Raman spectrometry). Textural equilibrium of chlorite and quartz was a pre-requisite and the chemical composition of chlorite was determined. The chlorite analyzed had a range in Fe/Mg varying between 0.35 and 0.7. Except for pure Mg-chlorite, Fe–Mg substitution within the range measured does not change the oxygen isotope fractionation between quartz and chlorite measurably. The results support a linear correlation for chlorite–quartz fractionation over the temperature range given by this study (240–550 °C):

$$1000\ \ln\alpha = -0.01323(\pm 0.002) \times T\,(^\circ\mathrm{C}) + 10.97(\pm 0.92)$$

The presently established geothermometer can be applied to quartz–chlorite fractionations in low-grade metamorphic rocks and may be extrapolated to diagenetic systems.

## 1. INTRODUCTION

Oxygen isotope analyses of natural minerals and the oxygen isotope fractionations between cogenetic minerals as well as between minerals and water, have played a major role in understanding geological processes. Stable oxygen isotope measurements are widely applied to geothermometry (e.g., Kyser et al., 1981; Burkhard et al., 1992; Kirschner et al., 1995; Valley, 2001; Skora et al., 2011; Lacroix et al., 2012; Potter et al., 2012; Sindern et al., 2012) and are used to constrain the types (origins) of fluids involved in fluid–rock interactions (e.g., Taylor, 1977; Bradbury and Woodwell, 1987; Rye and Bradbury, 1988; Fitz-Diaz et al., 2011; Potter et al., 2012; Bergman et al., 2013).

Chlorite and quartz are common minerals in rocks influenced by diagenesis, but also in low- to high-grade metamorphic rocks, as well as in many hydrothermal ore deposits. Often, the presence of these minerals in veins and rocks is directly related to fluid transport and fluid–rock-interactions. The common occurrence of this mineral assemblage covers a large range of pressure and temperature, with temperatures of <200 °C up to 650 °C.

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The quartz–water oxygen isotope fractionation has been experimentally (e.g., Clayton et al., 1972; Matsuhisa et al., 1979; Zhang et al., 1989; Hu and Clayton, 2003), empirically or semi-empirically (e.g., Bottinga and Javoy, 1973; Sharp and Kirschner, 1994) and theoretically (e.g., Shiro and Sakaï, 1972; Zheng, 1993) determined. However, the situation is different for chlorite–water or chlorite–mineral oxygen isotope fractionations at low as well as high temperature conditions. There is only one experimental calibration for oxygen isotope fractionations between chlorite and water made in the temperature range from 170 to 350 °C (Cole and Ripley, 1999) as well as an empirical calibration from Wenner and Taylor (1971).

The problem at low temperatures is that the exchange rates for most minerals are too slow to be investigated by laboratory experiments and that the synthesis of most silicates at such temperatures is difficult, if not impossible (e.g., Sharp, 2009). Given these problems, another approach is to use nature as the "laboratory" (e.g., Bottinga and Javoy, 1973; Sharp and Kirschner, 1994; Valley et al., 2003). In this study an empirical approach is taken to compare the oxygen isotope fractionations between quartz and chlorite to temperatures obtained independently from geologic or field constraints, as well as mineralogical–petrological constraints. In addition, this calibration is compared to existing estimates on quartz–chlorite oxygen isotope fractionations based on experimental and theoretical studies and is discussed in the light of possible retrograde diffusion effects and possible mineral–fluid exchange.

## 2. SAMPLES AND ANALYTICAL METHODS

### 2.1. Sources of samples

In order to calibrate the new oxygen isotope fractionation curve between quartz and chlorite samples in different areas where quartz and chlorite have been noted to be abundant and in textural equilibrium have been collected, notably where independent temperature estimates were available or could be made. The independent temperature estimates for the chosen localities are presented in Table 1. They are based on fluid inclusion homogenization temperatures, mineral assemblages and petrology of the host rocks to the veins, thermodynamic modeling, oxygen isotope thermometry on other mineral phases, and Raman spectrometry. The localities were selected based on the convergence of several thermometric methods and/or where textural and mineralogic evidence in the veins corresponds to temperature estimates based on regional geologic temperature conditions. 13 different localities in the Alps, Pyrenees, Ardennes, and Corsica were selected for this study (see also the supplementary data to this manuscript).

In the Alps the samples are from an eclogite of the Saint Marcel Valley (Martin et al., 2008), from a blueschist of the Queyras valley (Schwartz et al., 2009, 2013), from the Mont Blanc Massif (Rolland et al., 2003; Rossi et al., 2005), and the Aar (Goncalves et al., 2012) and Argentera (Corsini et al., 2004) massifs. In the Pyrenees, samples are from the Néouvielle massif (Henderson and McCaig, 1996), Pic Port Vieux (Grant et al., 1990), Trimouns talc quarry (Moine et al., 1989; Boulvais et al., 2006) and the Monte Perdido thrust unit (Lacroix et al., 2012). In the Ardennes, samples come from the Stavelot massif (Schroyen and Muchez, 2000).

In most samples, chlorite and quartz occurred in veins, as cement and/or as part of the metamorphic assemblage in the lithologies. Special attention was placed on rock and mineral textures in order to avoid using samples with the minerals of interest presenting textural disequilibrium. Textural equilibrium is generally supported by interdigitated mineral textures in veins (Fig. 1A; supplementary Fig. S1) or by the presence of vermicular chlorite inside quartz grains (Fig. 1B; Fig. S1). For metamorphic rocks, both minerals demonstrate synkinematic textures, which also argues for textural equilibrium.

### 2.2. Chemical composition of chlorite

The chemical composition (Si, Fe, Mg, Mn, Al, Na, Ca, Ti, and K) of selected chlorites was analyzed using a JEOL electron microprobe equipped with five X-ray spectrometers at the University of Lausanne. The microprobe was operated using 20 kV of excitation potential, 10 nA of current intensity and a beam diameter of 6 μm. The standards used were orthoclase (K), albite (Na), andalusite (Al), forsterite (Mg), fayalite (Fe, Si), wollastonite (Ca), a chromium oxide (Cr), and a metal of MnTi (Mn and Ti). All analyses were recalculated as chlorite structural formulae on the basis of 14 oxygen equivalents and assuming all iron to be $Fe^{2+}$ (Table 2).

### 2.3. Oxygen isotope compositions of quartz and chlorite

Samples were crushed and sieved to pass a size fraction of 150–300 μm. Samples were then washed in distilled water and ethanol to remove fine powder and reduce the static magnetic effect. Quartz and chlorite from dried samples have been separated using a Frantz magnetic separator and hand-picked in order to obtain fractions as pure as possible (>95%). Quartz–chlorite pairs were analyzed for their oxygen isotope compositions at the stable isotope laboratory of University of Lausanne (Table 1) using a $CO_2$-laser fluorination line coupled to a Finnigan MAT 253 mass spectrometer, using a method similar to that described by Sharp (1990) and Rumble and Hoering (1994) and described in more detail in Kaseman et al. (2001). Between 0.5 and 2 mg of sample was loaded onto a Pt sample holder. Samples were dried in an oven for 24–48 h at 180 °C in order to remove potentially adsorbed water and then pumped out to a vacuum for at least 10 h. After several cycles of pre-fluorination, samples were heated with a $CO_2$-laser in 50 mbars of pure $F_2$. Excess $F_2$ is separated from the $O_2$ by conversion to $Cl_2$ using KCl held at 150 °C. The extracted $O_2$ is collected on a molecular sieve and expanded into the inlet of the gas source mass spectrometer. Oxygen isotope compositions are given in the standard δ-notation, expressed relative to VSMOW in permil (‰). Replicate oxygen isotope analyses of the standard used (LS-1 qtz) has an average precision of ±0.1‰ for $\delta^{18}O$.