

Stable oxygen isotope fractionation between smithsonite and fluid in the temperature range 25 and 80 °C

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INTRODUCTION & METHOD

Owing to the large fractionation between carbonate minerals and aqueous fluids with respect to their ¹⁸O/¹⁶O composition (i.e. $\Delta^{18}\text{O}_{\text{solid-water}} \sim 30\text{‰}$), the oxygen isotope composition of carbonates has been a fundamental tool for the estimation of mineral formation temperature and/or fluid origin by Earth scientists. In this study we synthesized smithsonite at the temperature range between 25 and 80 °C and we report the temperature dependence of oxygen isotope distribution between this mineral phase and the aqueous fluid. Our experimental setup can be seen in Fig. 1

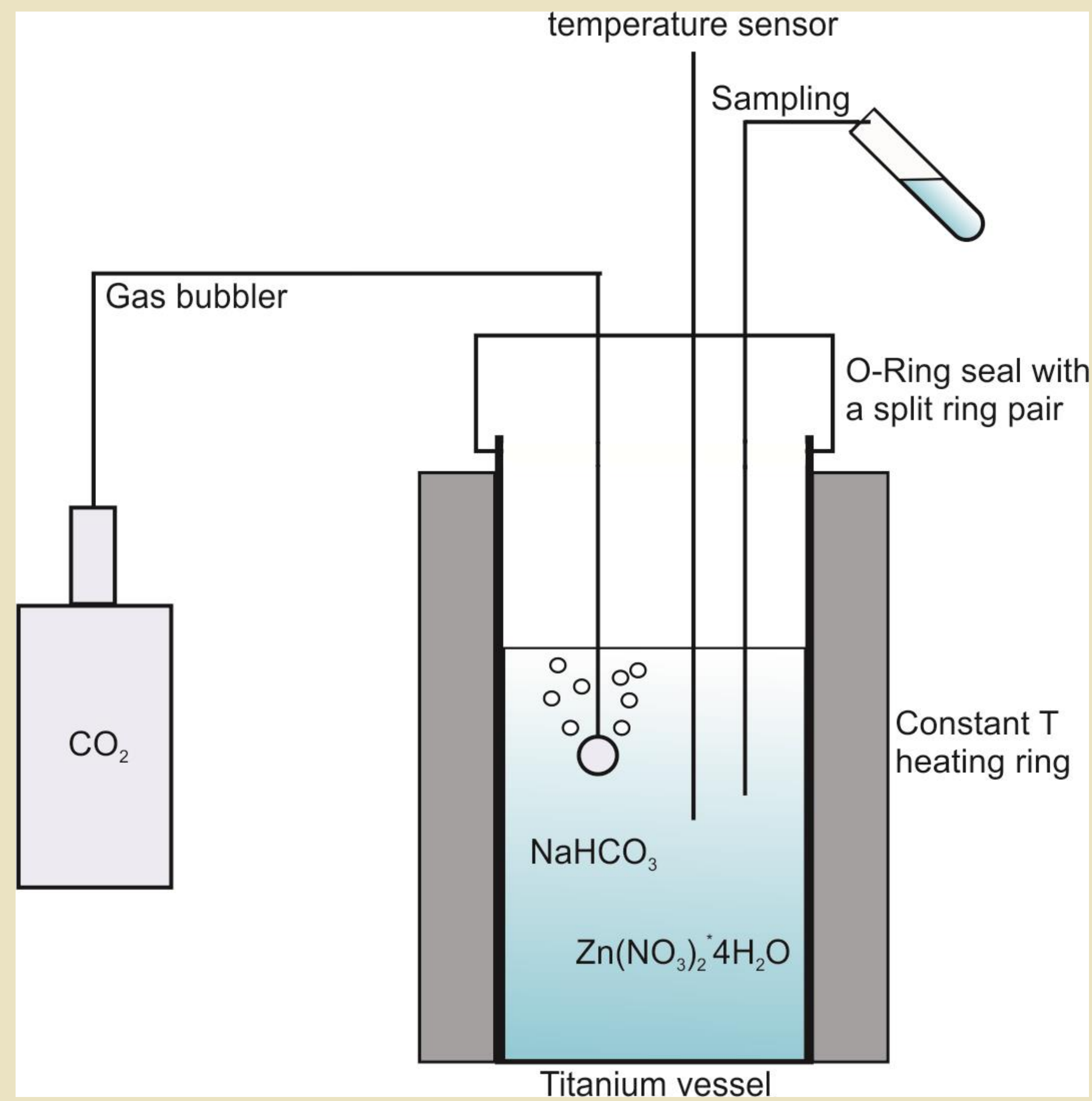


Fig 1. Experimental Setup

Ref.

- [1] Chacko & Deines (2008) *Geochim. Cosmochim. Acta*, **72**, 3642-3660.
- [2] Gilg et al. (2003) *Geochim. Cosmochim. Acta*, **67**, 21, 4049-4055.
- [3] Kim et al. (2015) *Geochim. Cosmochim. Acta*, **158**, 276-289.

XRD ANALYSIS

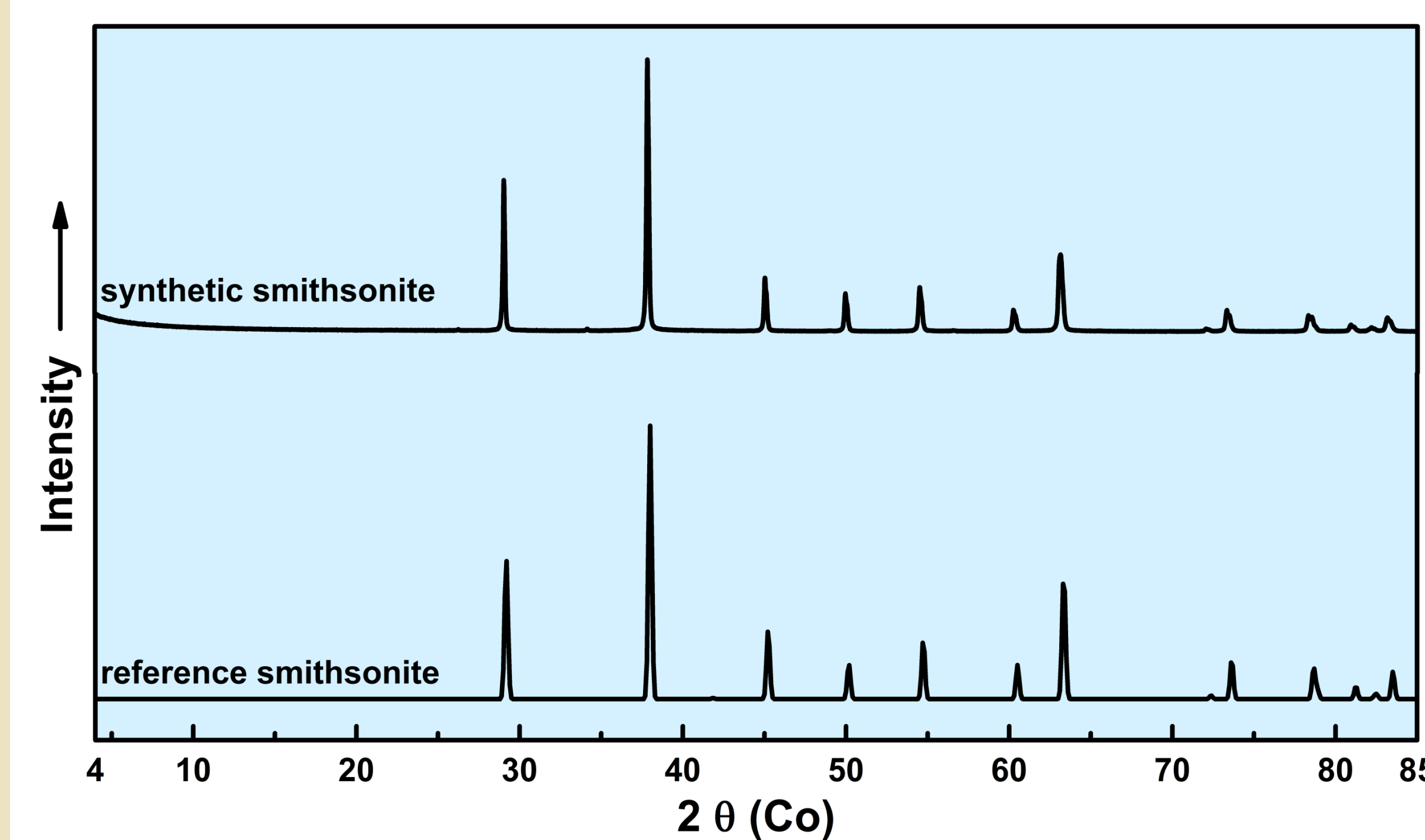
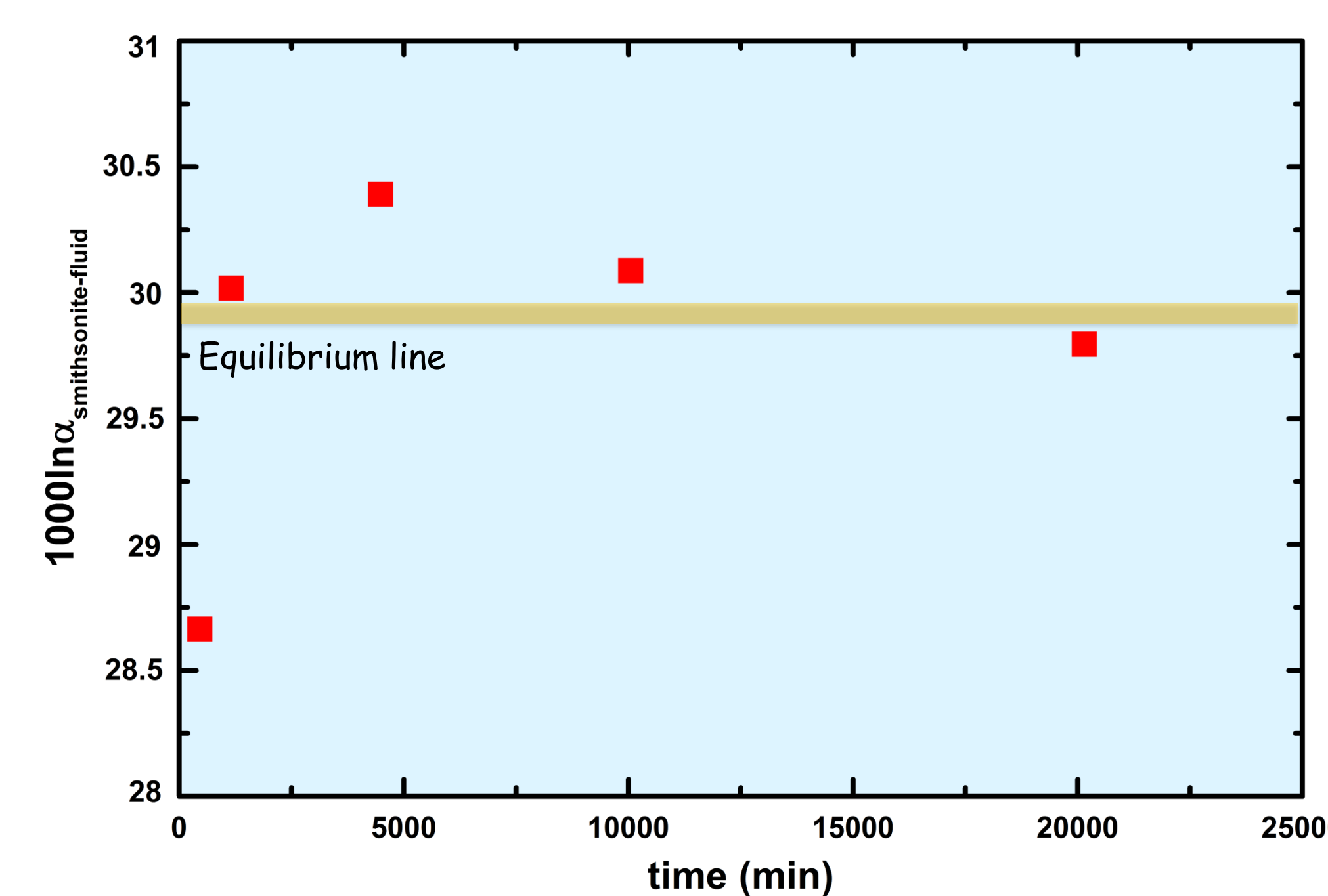


Fig 2. Typical X-ray diffraction pattern of synthetic smithsonite powder precipitated during this study at 10 pCO₂ and 25 °C after 8 h incubation compared to reference Smithsonite material (PDF-number: 01-083-1765 8-449)

TEMPORAL EVOLUTION OF $1000\ln\alpha_{\text{smithsonite-fluid}}$

The temporal evolution of the $1000\ln\alpha_{\text{smithsonite-fluid}}$ value over 14 days of experimental runs during this study as it can be seen in Fig. 3 suggests that the achievement of isotopic equilibrium is not instant at 25 °C, but requires substantial time, despite the fact that pH of the reactive fluid is low and CO_{2(aq)} is the predominant aqueous carbonate phase.



The enrichment of ¹⁶O in the solid phase at the initial stages of the experiment likely stems from sluggish exchange kinetics imposed by the absence of mechanical mixing in the setup used in this study.

Fig 3. Temporal evolution of the $1000\ln\alpha_{\text{smithsonite-fluid}}$ value for experiments conducted at 25 °C. Analytical error is within the symbol.

OXYGEN ISOTOPE FRACTIONATION

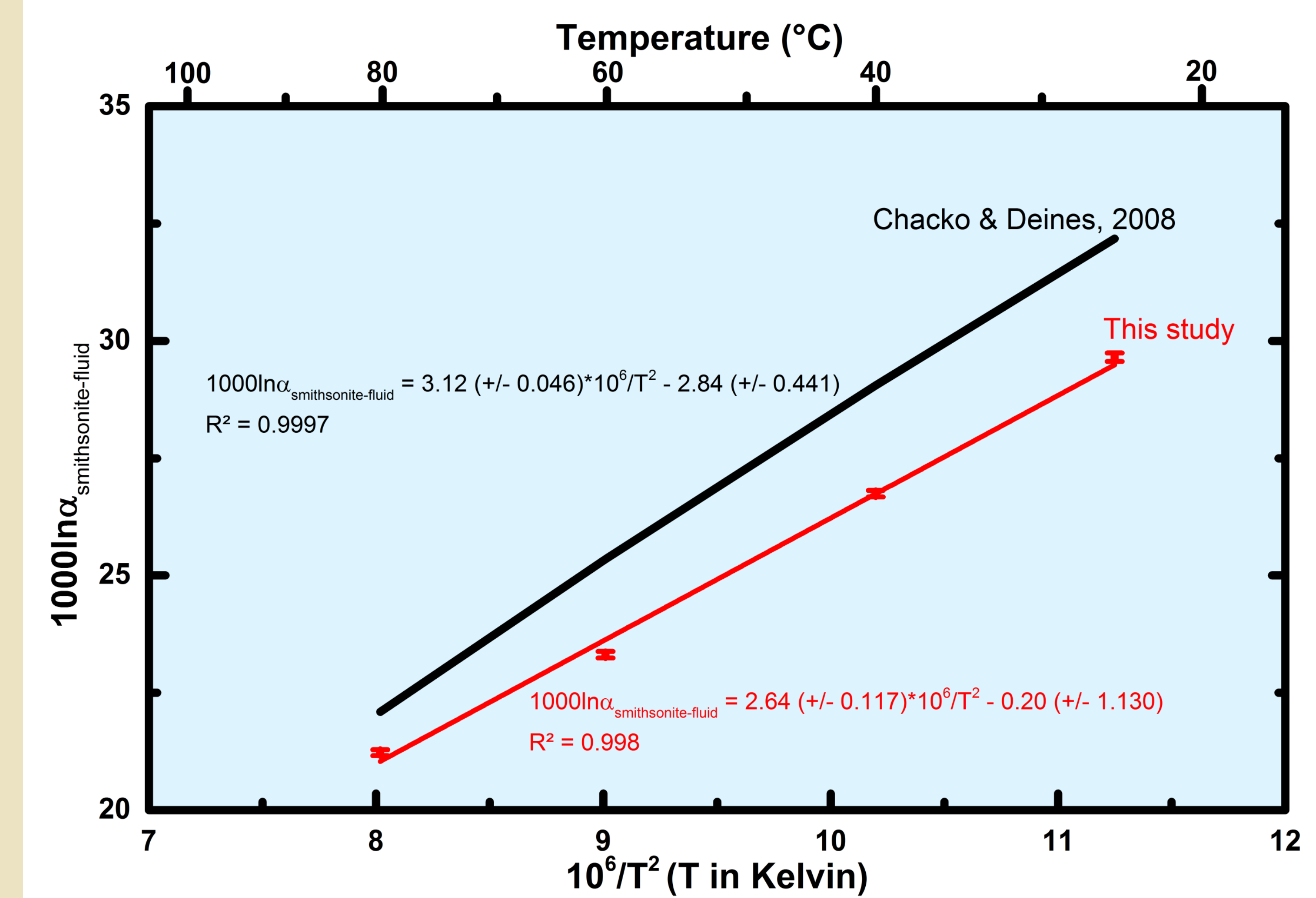


Fig 4. Oxygen isotope fractionation between smithsonite and fluid in the temperature range 25 and 80 °C estimated using a) a theoretical calculation after [1] and b) measured in this study [2] and [3].

Our experimental findings indicate a strong temperature control on the $1000\ln\alpha_{\text{smithsonite-fluid}}$ in the temperature range between 25 and 80 °C as it is illustrated in Fig. 4. The relation between temperature and isotopic fractionation can be described by:

$$1000\ln\alpha_{\text{smithsonite-fluid}} = 2.64 \times 10^6/T^2 - 0.20; R^2 = 0.998 \quad (1)$$

The measured fractionation as it is defined by Eq. 1 suggest less ¹⁸O enrichment in smithsonite compared to that established earlier by [1] based on first principle lattice dynamics simulations.