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Effect of growth rate and pH on Li isotope fractionation during its incorporation in calcite

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Abstract

Lithium isotope compositions were determined for synthetic calcite and fluid, reported in Fuger et al. (2019). Calcite was precipitated at 25°C, and mineral growth rate and pH varied within the range of $10^{-8.1} \leq r_p \text{ (mol m}^{-2} \text{ s}^{-1}) \leq 10^{-7.2}$ and $6.3 \leq \text{pH} \leq 9.5$, respectively. At pH = 8.25 ± 0.15 , the $\Delta^7\text{Li}_{\text{calcite-fluid}} = \delta^7\text{Li}_{\text{calcite}} - \delta^7\text{Li}_{\text{fluid}}$ value of $-2.76 \pm 0.22 \text{ ‰}$ (n=4) was yielded when calcite growth rate was lower than $\sim 10^{-7.7} \text{ (mol m}^{-2} \text{ s}^{-1})$. As calcite growth rate increased, $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values progressively decreased to about -4.5 ‰ . The dependence of Li isotope fractionation on calcite growth rate is described by the surface reaction kinetic model developed by DePaolo (2011). In this model the equilibrium and kinetic isotope fractionation factors obtain values of $-2.7 \pm 0.1 \text{ ‰}$ and $-8.8 \pm 0.1 \text{ ‰}$, respectively. In addition, for experiments performed under similar surface-normalized growth rate of $10^{-7.7 \pm 0.2} \text{ (mol m}^{-2} \text{ s}^{-1})$ a significant decrease in $\Delta^7\text{Li}_{\text{calcite-fluid}}$ from pH 9.5 to 6.3 was observed. These variations of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ as a function of pH for experiments performed under low degrees of solution saturation with respect to calcite point towards the incorporation of two or more Li-bearing species in the solid phase. Thus, the Li isotope composition of the solid reflects the abundance of these species, which depends on solution pH and fluid composition.

Overall the results of this study suggest that both calcite growth rate and pH are parameters that can significantly affect the measured Li isotope fractionation between calcite and fluid. The high sensitivity of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ to calcite growth rate observed in this study suggests that a high variability of $\delta^7\text{Li}_{\text{calcite}}$ in natural samples, such as foraminifera, brachiopods, and speleothems can be expected in natural environments. The implications for the potential use of elemental and isotope fractionation of Li during calcite formation are discussed in the light of reconstruction of paleo-environmental conditions.

Keywords: Li isotopes; calcite, Li isotope fractionation, pH effect, growth rate effect

1 INTRODUCTION

Owing to the large relative mass difference of $\sim 16.7\%$ between ^6Li and ^7Li the isotopic composition of Li in natural materials exhibits a significant variation on the order of $\sim 80\%$ (e.g., Tomascak et al., 2016). The large isotopic fractionation that is observed between solids and natural fluids at low temperatures is the main reason that Li isotopes have received growing attention, for example for continental weathering studies where they are used to constrain the intensity of continental silicate weathering and secondary mineral formation in the ocean (Chan and Edmond, 1988; Chan et al., 1992; Huh et al., 1998; 2001; Kisakürek et al., 2005; Vigier et al., 2009; Wimpenny et al., 2010; Pogge von Strandmann et al., 2012). Lithium is present at trace level concentrations in silicate minerals of continental rocks (e.g., Teng et al., 2008) and its major sources to the oceans are hydrothermal fluxes (e.g. Bray et al., 2001; Chan et al., 2002), continental weathering of the silicate rocks (Huh et al., 1998, Misra and Froelich, 2012) and groundwater discharge (Mayfield et al., 2021). Major sinks of oceanic Li are related to processes such as the neoformation of clays during sea-floor alteration and its incorporation in marine sediments (Chan et al., 1992; 2006; Vigier et al., 2008; Zhang et al., 1998).

The proportion of Li that is incorporated in marine carbonates is too small to be considered a significant Li sink from oceanic water, as is also inferred by the low partitioning coefficient of Li in calcite ($D_{\text{Li}}^* \leq \sim 10^{-3}$; Marriott et al., 2004a; 2004b; Füger et al., 2019; Day et al., 2021). The presence of Li in natural carbonates, however, has been argued to have the potential to provide insights into natural processes. For example, the Li/Ca ratios of marine calcite has been proposed as an environmental proxy of dissolved inorganic carbon (DIC), the degree of seawater saturation with respect to calcite, salinity, temperature and calcite precipitation rate, based the chemical composition of natural samples (Hall and Chan, 2004; Vigier et al., 2015; Lear et al., 2010; Marriott et al., 2004b; Delaney et al., 1985; 1989; Marriott et al., 2004a, Dellinger et al., 2018; 2020; Gaspers et al., 2021). The large number of proposed proxies based on the Li content of calcite suggests that either Li incorporation in calcite is controlled by biological processes and as such requires species-specific calibrations or that more than one process may affect its incorporation in calcite. The latter observation is

supported by the results of Fuger et al. (2019) who observed large variation in Li distribution coefficients between calcite and solution as a function of both growth rate and pH when surface-normalized growth rate was kept constant for minerals growing in the range $6.3 \leq \text{pH} \leq 9.5$. These authors argued that the formation of $>\text{LiHCO}_3^\circ$ surface complex on growing calcite is the key limiting step for Li incorporation in calcite, considering that the replacement of Ca^{2+} with Li^+ requires charge balance. If this mechanism holds true, then the Li content and Li/Ca ratio can be affected both by mineral growth rate and chemical composition of the forming fluid, considering that Li in the aqueous phase occurs in the aqueous phase mainly as Li^+ (aq), compared to other ions such as Ca and Mg which readily form complexes with organic and inorganic ligands.

The behavior of Li isotopes in calcite can provide new constraints on the incorporation mechanism of Li in this mineral phase. To date, Li isotope fractionation between CaCO_3 minerals and the fluid from which they form are rare in the literature. Earlier work has shown that Li isotope fractionation between inorganic calcite and solution is not significantly influenced by temperature (Marriott et al., 2004a; Day et al., 2021), while it is affected by the mineralogy of the CaCO_3 phase formed (Marriott et al., 2004b). These results are consistent with the variation in the Li isotope composition of biominerals with different CaCO_3 mineralogy such as shallow-water and deep-sea corals, foraminifera shells, mollusks, brachiopods and echinoderms (e.g. Rollion-Bard et al., 2009; Hathorne and James, 2006; Vigier et al., 2015; Dellinger et al., 2018), suggesting that the bonding environment of Li in calcite and aragonite is likely different. This is further supported by the recent work of Pogge von Strandmann et al. (2019), that has shown a significant difference in $\delta^7\text{Li}$ of bulk marine pelagic carbonate of aragonitic and calcitic composition. Despite the difference in $\delta^7\text{Li}$ values between calcite and aragonite, changes in Li isotope compositions due to other physicochemical parameters for which Li content has been proposed as a proxy appear to be contradicting. For example Rollion-Bard et al. (2009) demonstrated that Li isotope systematics of shallow-water and deep-sea corals are not affected by pH and pCO_2 changes of past seawater, whereas Vigier et al. (2015) suggested that Li isotope compositions in foraminifera shells can be used as a paleo-

ocean DIC indicator. In contrast, a recent study by Roberts et al. (2018) demonstrated a correlation of Li isotope fractionation in benthic foraminifera calcite with the pH of the culture medium. In this study a pH increase from 7.9 to 8.6 results in a decrease of the $\Delta^7\text{Li}$ value between the cultured *A. lessonii* and the growth medium of about 2.8‰ arguing for the use of Li isotopes as a pH proxy tool.

In the present study we explore the mechanisms controlling Li isotope fractionation during the growth of calcite, in abiotic experiments conducted under tightly controlled physico-chemical conditions of growth rate and pH. This study is based on an earlier work by Fuger et al. (2019) which focused on elemental distribution of Li between calcite and solution and which showed that the incorporation of Li into calcite is affected by both calcite growth rate and pH of the forming solution. Fuger et al. (2019) argued that the elevated concentration of Li in the precipitated calcite at increasing mineral growth rate, is associated with an increase of defect sites on the growing mineral surface. Furthermore, Fuger et al. (2019) argued that a surface complex of Li^+ with HCO_3^- is charge balancing the Li^+ ion at the calcite surface during a coupled incorporation as $>\text{LiHCO}_3^\circ$. This is well supported by the dependence of Li partitioning coefficient in calcite on pH of the forming fluid. In the present study, we address the Li isotope fractionation between calcite and solution for calcite formed at selected growth rates ($10^{-8.1} \leq r_p \text{ (mol m}^{-2} \text{ s}^{-1}) \leq 10^{-7.2}$) and pH conditions ($6.3 \leq \text{pH} \leq 9.5$) in order to extend the existing knowledge on Li isotope fractionation during calcite formation.

2 METHODS

2.1 Experimental set-up

Lithium co-precipitation experiments with calcite were performed using a mixed-flow reactor system described in Fuger et al. (2019). Briefly, calcite overgrowth was induced by simultaneous pumping of two separate inlet solutions into the reactor with the aid of a peristaltic pump (see Fig. 1 in Fuger et al., 2019). The first inlet solution contained CaCl_2 and LiCl , while the second contained Na_2CO_3 . The LiCl solution used in all runs originated from a single stock solution. The concentration of CaCl_2 in the inlet solutions varied from 0.025 to 0.1 M and it was

kept equal to that of Na_2CO_3 in the second inlet solution in all runs. Before the onset of each run the initial reactor fluid contained 0.5 L of a 0.3 M NaCl solution that was equilibrated with calcite at the predefined pH conditions. This concentration of background electrolyte allowed for both a large variation in the inlet solution concentrations without altering ionic strength and a robust estimation of aqueous speciation using the extended Debye-Hückel equation. Every reactor was equipped with a floating Teflon-coated stir-bar typically operating at 250 rpm. Shortly before the onset of each run synthetic calcite seeds were introduced in the reactor. Details for the amount of seed material used in each run are given in the electronic Annex (Table S1). During the course of a run the pH of the reactive solution was controlled by the continuous bubbling of water-saturated CO_2 , N_2 and/or air gas mixtures and remained constant during the course of a run (Fig. 1A) that lasted for 7 days. For experiments conducted at $\text{pH} > 9.0$, constant pH was achieved by titration of 0.5 M NaOH into the reactor vessel. The volumes of the reactor solution were kept constant within $\pm 4\%$, by removing a volume from the reactor equal to the volume of the inflowing solution every 24 h. Immediately after sampling, the solution was filtered through a 0.2 μm Millipore cellulose acetate syringe filter for chemical and isotopic analyses. At the end of the experimental runs, the solution was separated from the solid phase via vacuum filtration using a 0.2 μm filter (Millipore, cellulose acetate). The solids were rinsed with deionized water and dried at 40 °C.

2.2 Chemical and mineralogical analyses

Chemical composition of solids and reactive solutions was measured using inductively coupled plasma optical emission spectrometry (ICP-OES Optima 8300 DV, Perkin Elmer). The alkalinity of the reactive solutions was measured by standard HCl titration using an automated Schott TitroLine alpha plus titrator with an uncertainty of $\pm 2\%$. The pH of the reactive solutions was measured in-situ using a SenTix® 945 pH gel electrode from WTW with a precision of ± 0.04 units. The mineralogic composition of solid phases was characterized using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR; Perkin Elmer Spektrum 100), X-ray diffraction (XRD; PANalytical X'Pert PRO diffractometer) and scanning

electron microscopy (SEM; ZEISS DSM 982 Gemini). Micrographs of the seed material and the overgrowths are given in Füger et al. (2019). The specific surface area of seed material and selected solids collected at the end of the experimental runs was determined using a Quantachrome Gas Sorption system and 11-point krypton adsorption method (Brunauer et al., 1938) with an uncertainty of $\pm 10\%$. The chemical composition of the reactive solution at steady-state conditions together with alkalinity and pH were used to estimate saturation indices with respect to calcite. Aqueous speciation and degree of saturation of the reactive fluid with respect to calcite were estimated using the PhreeqC software together with its MINTEQ.V4 database (Parkhurst and Appelo, 1999).

2.3 Lithium isotope analyses

The chromatographic separation of Li from matrix elements from liquid and solid samples followed a two-stage analytical protocol detailed in Magna et al. (2004; 2006). Briefly, 0.5-2.5 mL aliquots of liquid samples were evaporated to dryness and re-dissolved in 0.5 mL of a mixture of 0.67M HNO₃–30% methanol for loading onto the first-step ion exchange resin. The first column used 2.1 mL of a cation-exchange resin BioRad AG50W-X8 (mesh 200–400) and a mixture of 1M HNO₃–80% methanol to isolate Li. The collected Li fractions were evaporated to dryness and re-dissolved in 0.2 mL 0.2M HNO₃ for the second-step chemistry. The second stage employed 0.6 mL of a cation-exchange resin BioRad AG50W-X12 (mesh 200–400) and 0.5M HNO₃ to obtain a clean Li fraction. All reagents used were Teflon double-distilled and 18.2 M Ω .cm deionized water was used for the entire laboratory routines. The methodology used during this study has been reported in detail elsewhere (Magna et al., 2004). It ensures full recovery of Li (>99%) to avoid chromatography-based Li isotope fractionation which would severely compromise true ⁷Li/⁶Li (cf. Košler et al., 2001). Total procedural blank is <20 pg Li which is negligible compared to 10–100 ng Li from the samples.

Lithium isotope measurements were conducted at the Institut de Physique du Globe de Paris (IPGP) and the Czech Geological Survey (CGS), respectively. At IPGP, Li isotope ratios were determined using a Neptune (Thermo Scientific) MC-ICP-MS coupled with an APEX-HF

desolvation system and measurements were typically performed on solutions with a Li concentration of 20 – 30 ppb. Each sample was measured 3 times using a standard-sample bracketing (SSB) approach. At the Czech Geological Survey, Li isotope measurements were carried out using a Neptune MC-ICP-MS (Thermo Scientific), connected to an Aridus II desolvating unit (CETAC) and 30 µl/min PFA nebulizer. A high-efficiency skimmer X-cone was used. The resulting ^7Li signal was typically 600–800 V/ppm. For Li isotope measurements, the SSB technique was employed. Lithium isotope ratios are reported in conventional δ notation relative to the L-SVEC Li-isotope standard (Flesch et al., 1973) and calculated as:

$$\delta^7\text{Li} (\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000. \quad (1).$$

The uncertainties are reported as the 2-standard deviation (2SD). The reliability of the entire analytical and instrumental protocol used and the comparability of results between IPGP and CGS were assessed by the analysis of reference materials IAPSO (seawater, OSIL, Havant, UK; $\delta^7\text{Li} = 31.00 \pm 0.12\text{‰}$) and NASS-6 (National Research Council of Canada, Ottawa, Canada $\delta^7\text{Li} = 30.94 \pm 0.12\text{‰}$) and the Li stock solution. Lithium isotope ratios of these materials are reported in Table 1 and are consistent with literature (e.g., Kuessner et al., 2019; Mayfield et al., 2021).

3 RESULTS

3.1 Mineralogical and chemical characterization of precipitated solids and reactive fluids

The solids collected at the end of each run yielded X-ray diffraction patterns similar to those of the seed material, and are consistent with that of calcite (Füger et al., 2019). The amount of overgrowth was more than 20% of that of seed material in all the runs (Table S1). The collected patterns do not suggest the presence of other CaCO_3 polymorphs such as aragonite. The specific surface area of selected samples was similar, within analytical uncertainty, to that of calcite seeds (Table S1). Over the course of an experimental run chemical steady-state concentrations with respect to Ca were achieved between 1000 and 3000 min depending on

the applied pumping rate, whereas Li concentrations remained constant within the duration of each run, as is apparent from Fig. 1A for experiment CaLi3_40. Calcite growth took place in the pH range $6.3 \leq \text{pH} \leq 9.4$ but within a single run the maximum pH variation observed was lower than 0.09 units. Average pH values for the runs of this study and variations observed within a run are listed in Tables 1 and S1.

The rates of calcite growth in this study were estimated based on mass balance considerations. The number of moles of Ca introduced into the reactor per unit time was corrected for the number of moles of Ca removed over the same period of time via sampling. Under chemical steady-state conditions calcite growth rate, r_p can be estimated as:

$$r_p = \frac{n_{Ca(add)} - n_{Ca(rem)}}{86400} / S \quad (2)$$

where n stands for the number of moles of Ca added into the reactor and removed from the reactor within 24 h, S denotes the total calcite surface (m^2) and 86400 stands for the number of seconds in 24 h (Voigt et al., 2017; Mavromatis et al. 2019). The total surface area was corrected for the amount of overgrowth but not for changes in the specific surface of the bulk solids collected from the reactor at the end of each run because the measured reactive surface of selected solids was within uncertainty the same to that of calcite seeds (Table S1). Growth rates are expressed in $\text{mol m}^{-2} \text{s}^{-1}$ and, based on the increase of mass over the duration of a run, growth rate has an uncertainty better than $10^{\pm 0.15} \text{ mol m}^{-2} \text{s}^{-1}$. As can be inferred from Eq. 2 growth rate does not take into account the incorporation of Li into the precipitated calcite as the respective Li amounts are negligible compared to Ca. The obtained overall variation in growth rates in all of the experiments falls within the range $10^{-8.2} \leq r_p \leq 10^{-7.1}$ (see Table 1). The apparent distribution coefficient of Li in calcite overgrowths has been calculated following Fuger et al. (2019) using steady-state Ca and Li concentrations as:

$$D_{Li^+}^* = \frac{(c_{Li}/c_{Ca})_{calcite}}{(m_{Li^+}/m_{Ca^{2+}})_{solution}} \quad (3)$$

where c stands for the concentration of the metal ions in calcite, m_{Li^+} and $m_{Ca^{2+}}$ are the molar concentration of Li^+ and Ca^{2+} ions in the aqueous phase, respectively. Calcite seeds did not contain measurable amounts of Li and as such no correction was applied for the estimation of the apparent Li distribution coefficient using Eq. (3). The estimated $D_{Li^+}^*$ values used in this study originate from Fuger et al. (2020) and are reported in Table 1.

3.2 Lithium isotope composition and isotope fractionation between calcite and fluid

The measured Li isotope composition of aqueous fluids (δ^7Li_{fluid}) and precipitates are reported in Table 1. Note here that sub-samples of reactive fluids analyzed for their Li isotope composition have been collected at different time steps of the experimental runs (Table 1). The Li isotope compositions of the LiCl stock solution ($8.67 \pm 0.16 \text{ ‰}$), the initial solution in the reactors ($8.59 \pm 0.16 \text{ ‰}$) and the reactive solution ($8.57 \pm 0.09 \text{ ‰}$) at the four different pH values of the experimental runs examined in this study exhibit variation that is lower than the analytical precision of the measurement (Fig. 1B). The small variation in δ^7Li of the fluid samples, within analytical uncertainty, is consistent with the low distribution coefficient of Li in calcite (Table 1). This implies that there was negligible temporal δ^7Li variation of the reactive fluid from which calcite formed in the experiments.

The Li isotopic composition of calcite overgrowths ranged between $3.29 \pm 0.31 \text{ ‰}$ (experiment CaLi12_100) and $6.79 \pm 0.28 \text{ ‰}$ (experiment CaLi7_50). Since calcite seeds did not contain measurable amounts of Li, the apparent fractionation between calcite overgrowths and aqueous Li has been calculated as the respective difference between the isotope composition of the two phases according to the equation:

$$\Delta^7Li_{calcite-fluid} = \delta^7Li_{calcite} - \delta^7Li_{fluid} \quad (4)$$

In all experiments, calcite overgrowths exhibited a preferential incorporation of 6Li compared to that of the forming solution (Table 1), consistent with studies of natural calcite (e.g., Marriott et al., 2004a; Dellinger et al., 2018; Washington et al., 2020). We note here that for the

estimation of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values in all runs the average $\delta^7\text{Li}_{\text{fluid}}$ value of 8.57 ± 0.09 ‰ was used. As plotted in Fig. 2A for calcite growth experiments performed at $\text{pH} = 8.25 \pm 0.15$, the measured $\Delta^7\text{Li}_{\text{calcite-fluid}}$ exhibits a constant value of -2.76 ± 0.22 ‰ ($n=4$), when calcite growth rate is lower than $\sim 10^{-7.7}$ ($\text{mol m}^{-2} \text{s}^{-1}$). Under the same pH conditions, as growth rate increases, $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values become progressively more negative reaching a value of -4.51 ‰ in experiment 5_80 conducted at a growth rate of $10^{-7.2}$ ($\text{mol m}^{-2} \text{s}^{-1}$). Overall, the dependence of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ on the calcite growth rate in the experiments of this study where $-7.7 \leq \text{Log}r_p$ ($\text{mol m}^{-2} \text{s}^{-1}$) ≤ -7.2 and can be described by the linear equation:

$$\Delta^7\text{Li}_{\text{calcite-fluid}} = -3.00 (\pm 0.43) \times \text{Log}r_p - 25.88 (\pm 3.22); R^2=0.83 \quad (5)$$

The variation of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values as a function of growth rate can additionally be modelled in terms of deviation from near chemical equilibrium values using the expression derived by DePaolo (2011). Initially this model used to describe Ca isotope fractionation during calcite growth under steady-state conditions with the assumption that the precipitation of this mineral follows a first order transition state theory (TST) law as:

$$a_{ss} = \frac{a_f}{1 + \frac{R_b}{R_{net} + R_b} \left(\frac{a_f}{a_{eq}} - 1 \right)} \quad (6)$$

The terms R_b and R_{net} in Eq. (6) denote backward dissolution rate and net precipitation rate, respectively, whereas a_f and a_{eq} represent the kinetic and equilibrium isotope fractionation factors, respectively, associated with calcite precipitation. The same equation has been used to describe isotope fractionation of trace divalent cations (Me^{2+} , e.g. Ba^{2+} , Sr^{2+} , etc.) during their co-precipitation with CaCO_3 minerals under steady-state conditions (Mavromatis et al., 2020). This approach assumes the formation of a diluted solid solution with composition of Ca_{1-x} .

$x\text{Me}_x\text{CO}_3$ whose precipitation rate under chemical steady-state conditions is equal to that of the CaCO_3 phase.

Additionally, in experiments where calcite was grown at a constant growth rate of $10^{-7.8 \pm 0.3} \text{ mol m}^{-2} \text{ s}^{-1}$, the $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values increase from $-5.28 \pm 0.20 \text{ ‰}$ at pH 6.3 to $-1.78 \pm 0.20 \text{ ‰}$ at pH ~ 9.6 (Fig. 3) following a linear trend that can be described using the equation:

$$\Delta^7\text{Li}_{\text{calcite-fluid}} = 0.94 (\pm 0.14) \times \text{pH} - 10.39 (\pm 1.13); R^2 = 0.90 \quad (7).$$

Note here that Eq. (7) is valid for $6.3 \leq \text{pH} \leq 9.5$ and for calcite formed from aqueous fluid with a composition similar to that applied in this study.

4 DISCUSSION

4.1 Effect of calcite growth rate on Li isotope fractionation

The constant $\Delta^7\text{Li}_{\text{calcite-fluid}}$ value of $-2.76 \pm 0.22 \text{ ‰}$ in experiments conducted at growth rate lower than $10^{-7.7} \text{ (mol m}^{-2} \text{ s}^{-1})$ and similar pH conditions of 8.25 ± 0.15 , points towards isotope fractionation at near equilibrium conditions. Under isotopic equilibrium, the composition of the solid phase is not affected by the rate of attachment of the heavier or the lighter isotope on the growing crystal, because the net reaction rate of the forward (i.e. dissolution) and the backward (i.e. precipitation) reactions are equal, as has been formulated earlier within the framework of the transition state theory (TST; Lasaga, 1981; Aagaard and Helgeson, 1982; Oelkers, 2001; Schott et al., 2009). This is further supported by using Eq. (6) to calculate the Li isotope fractionation as a function of calcite growth rate (Fig. 2B). For this calculation, the backward calcite dissolution rate, R_b , was $2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ and the a_{eq} value derived for the estimates of this study for growth rate lower than $10^{-7.7} \text{ (mol m}^{-2} \text{ s}^{-1})$ was 0.9973 ± 0.0001 . The best fit with the experimental data was derived using an $a_f = 0.9912 \pm 0.0001$ and keeping the a_{eq} value constant. However, the R_b of $2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ is about half an order of magnitude lower compared to that proposed by Chou et al. (1989) for calcite dissolution in pure water at

circumneutral pH conditions and 25°C. This is a notable discrepancy considering that the R_b value should not be an adjustable parameter (DePaolo, 2011) and also is in direct contradiction with earlier studies modelling the incorporation of trace Me^{2+} in CaCO_3 minerals (e.g., DePaolo, 2011; Mavromatis et al., 2020). Similar variations of the R_b value compared to that proposed by Chou et al. (1989) have been reported during the modelling of other incompatible ions in calcite such as B (Farmer et al., 2019). Thus, we assign the observed discrepancy to the fact that incorporation of Li in calcite cannot be considered as the direct replacement of Ca^{2+} with Li^+ in the solid. Indeed, the incorporation of the monovalent Li^+ ion in calcite requires the additional presence of another ion that can compensate for the charge imbalance. Note also that if an R_b value of $6 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ is used in the TST model presented in Fig. 2B and consistent with that proposed by Chou et al. (1989), the best-fit is achieved with an $a_f = 0.980$. This would then be converted to $\Delta^7\text{Li}_{\text{calcite-fluid}} = -20\text{‰}$, which can be considered an unreasonable value that is not supported by experimental findings and/or natural studies.

At calcite growth rate $>10^{-7.7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values become progressively more negative with increasing growth rate, and as low as -4.5‰ (Fig. 2). This behavior is a typical feature during the formation of divalent cation carbonate minerals, where the solid phase exhibits an increasing enrichment in the lighter isotope with increasing mineral growth rate (Druhan et al., 2013; Steefel et al., 2014). A similarly increasing extent of Me^{2+} isotope fractionation during the departure from equilibrium conditions has been observed in other experimental studies where mineral growth rate has been strictly controlled. For example, increasing fractionation as a function of growth rate has been recorded for Ca in calcite (Tang et al., 2008), Mg in magnesite (Pearce et al., 2012), Ba in witherite (Mavromatis et al., 2016; Boettcher et al., 2018) and Sr in strontianite (Mavromatis et al., 2017a). This behavior is also valid during the incorporation of trace elements in carbonate minerals; for example, Sr incorporation in calcite (Böhm et al., 2012) and Ba incorporation in aragonite (Mavromatis et al., 2020) both exhibit increasing enrichments of the lighter isotopes in the solid phase at increasing mineral growth rates. Notably, the departure from near-equilibrium conditions during the incorporation of Me^{2+} in carbonate minerals does not result only in increasing extent of

metal isotope fractionation between the solid and the aqueous ion, but also results in decreasing fractionation with increasing growth rate. In the case of Mg and Ni incorporation in calcite, for example, isotope fractionation decreases at elevated growth rates (Alvarez et al., 2021; Mavromatis et al., 2013; Schott et al., 2014) a feature associated with the sluggish exchange of H₂O molecules between the bulk water and the hydration sphere of these divalent cations. Besides, similar kinetic effects are not strictly limited to Me²⁺ but have also been observed for oxyanions such as HBO₃⁻ (Farmer et al., 2019) and MoO₄²⁻ (Skierszkan et al., 2019).

The observed enrichment of the lighter isotopes during Me²⁺ introduction in the solid phase has been argued to be driven by the desolvation of the hydration sphere of the free metal aqueous ion (e.g. Pokrovsky and Schott, 2002; Hofmann et al., 2012; Böttcher, et al., 2018; Lammers et al., 2020; Alvarez et al., 2021). Indeed, the exchange rate of H₂O in the first hydration shell of the free ions follows an inverse power law (Hofmann et al., 2012), resulting in a progressive enrichment of the lighter isotope in the solid phase at increasing mineral precipitation rates. Based on the fit of Eq. (6) to the experimental data of this study, we argue that desolvation of the inner hydration sphere of aqueous Li ion is the process controlling the observed increasing kinetic isotope fractionation during Li incorporation in calcite (Fig. 2B). This is further supported by the α_f value used for the best-fit displayed in Fig. 2B (0.9912 ± 0.0001) which is in excellent agreement with that proposed by Hofmann et al. (2012) based on molecular dynamic simulations. Thus, a greater enrichment of ⁶Li in the solid phase can plausibly be observed, when calcite growth occurs at rates higher than those exploited in this study (i.e. $>10^{-7.2} \text{ mol m}^{-2} \text{ s}^{-1}$).

4.2 Effect of pH on Li isotope fractionation between calcite and fluid

A novel finding of this study is that $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values exhibit a quasi-linear correlation with pH for experiments conducted under similar surface-normalized growth rates ($10^{-7.7 \pm 0.2} \text{ mol m}^{-2} \text{ s}^{-1}$) as pH increases from ~6.3 to ~9.5. All these experiments exhibit low degrees of supersaturation of the fluid with respect to calcite (S_{calcite}) that in general does not exceed

values greater than 0.1 (Table S1) and likely reflects calcite formation at near isotopic equilibrium conditions. The pH dependence of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values (Fig. 3) is similar to that observed for the same set of experiments for the Li distribution coefficient as reported by Fuger et al. (2019). As can be seen in Fig. 4, $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values exhibit a tight correlation with the apparent Li distribution coefficients between calcite and fluid. The dependence of these two parameters can be described using the following equation:

$$\Delta^7\text{Li}_{\text{calcite-fluid}} = -1.75 (\pm 0.16) \times D_{\text{Li}}^* - 9.99 (\pm 0.60); R^2 = 0.88 \quad (8)$$

The similar behavior of Li isotope fractionation and elemental partitioning in calcite as a function of pH suggests that a common mechanism is controlling both processes. In the study of Fuger et al. (2019) it was argued that during the incorporation of Li in calcite at various pH conditions the positive charge excess is balanced by the presence of bicarbonate ion. These authors argued for the formation of $>\text{LiHCO}_3^0$ during the adsorption step of solutes on the crystal surface. Interestingly, a similar dependence exists between the activity of HCO_3^- (aq) and $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values (Fig. 5). At the highest pH at which calcite precipitated in this study (~ 9.5), both the activity of HCO_3^- (aq) and the measured $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values exhibit the highest values. The relationship between these two parameters for experiments conducted under similar surface-normalized growth rates (i.e. $10^{-7.7 \pm 0.2} \text{ mol m}^{-2} \text{ s}^{-1}$) can be described as:

$$\Delta^7\text{Li}_{\text{calcite-fluid}} = -2.22 (\pm 0.27) \times \text{Log} a_{\text{HCO}_3^-} - 8.78 (\pm 0.71); R^2 = 0.86 \quad (9)$$

Although Eq. (9) suggests a good correlation between $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values and $a_{\text{HCO}_3^-}$ the variation of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values in the absence of growth kinetic effects is rather unlikely to support the incorporation of only one species of Li, here LiHCO_3^0 , in calcite. The observed dependence on pH (Fig. 3) rather reflects the presence of two or more Li-bearing species in the forming solid. Indeed, if all calcite samples formed at $r_p < 10^{-7.7 \pm 0.2} \text{ (mol m}^{-2} \text{ s}^{-1})$ reflect formation at near isotope equilibrium conditions and in all these solids Li is present as one

species, the $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values should not exhibit variation with pH (Fig. 3), but rather obtain a similar value. Note here that Li in the aqueous phase occurs only as $\text{Li}(\text{H}_2\text{O})_4^+$ thus does not support changes in $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values due to aqueous complexation as it was earlier observed for other elements (e.g. B, Zn). Hence, the observed variations in $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values suggest that the incorporation of Li during calcite formation in experiments displayed in Fig. 3 occurs as two or more species whose relevant abundance in the solid control its Li isotope composition.

The presence of two or more Li species in the solid phase that is suggested here by the changes of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ value as a function of pH, indicates that the charge balance required for the presence of Li in calcite may be provided by different dissolved ions at different pH conditions (e.g. H^+ , OH^- , HCO_3^-). Thus, the potential presence of $>\text{LiHCO}_3^\circ$ during growth that has been earlier proposed by Fuger et al. (2019) may occur or prevail at a given pH conditions but not in the whole range from pH ~6.3 to ~9.5. This is not surprising considering that for monovalent ions a one-to-one substitution for Ca in the solid is unlikely to occur and charge balance is achieved from different surface species and/or their combination at different pH conditions. For additional information on the surface species of Li on calcite, a surface complexation model is needed. It is worth noting however that the presence of two or more Li-bearing species in the solid suggest that at different fluid compositions (e.g. seawater), $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values may be somewhat different to those obtained in this study, based on the bonding environment of Li in the solid.

Finally, it is interesting to note that the dependence of $\Delta^7\text{Li}_{\text{calcite-fluid}}$ on pH described with Eq. (7) exhibits opposite trend to that which has been described earlier by Roberts et al. (2018) for cultured *A. lessonii*. These authors argued that as pH increases from 7.9 to 8.6, changes in the second hydration sphere of Li^+ (aq) can increase the rates of desolvation of ^6Li leading to an enrichment in ^6Li of the solid. According to Roberts et al. (2018), this process occurs due to the formation of an outer sphere complex of Li^+ (aq) with OH^- (aq). Yet, the presence of LiOH° (aq) is rather unlikely to occur at circumneutral pH conditions (Baes and Mesmer, 1981). As discussed in section 4.1, ion desolvation is commonly associated with the dehydration of

the first, rather than second, hydration sphere of the aqueous ion prior to its attachment onto the mineral surface during mineral growth (Hofmann et al., 2012). Thus, the Li isotope fractionation observed by Roberts et al. (2018) may be also interpreted as the result of kinetic effects occurring at elevated growth rates imposed by the increase in pH. Note here however that Roberts et al. (2018) do not provide growth rate estimates for the cultured foraminifera.

4.3 Implications for the utility of Li isotope composition in natural calcite

The results obtained in this study indicate that the extent of Li isotope fractionation between calcite and the growth fluid can be significantly affected by two parameters, the rate at which calcite precipitated and the pH of the growth solution. According to our results (Figs. 2 and 3), variations in both these parameters result in measurable changes in $\Delta^7\text{Li}_{\text{calcite-fluid}}$. Indeed, a large increase in $\Delta^7\text{Li}_{\text{calcite-fluid}}$ of $\sim 5\text{‰}$ can be predicted by the obtained TST fit of our data, if growth rate increases by about two orders of magnitude (Fig. 2b). Notably, according to this fit, the isotope fractionation between Li in calcite and Li^+ (aq) will remain constant at ca. -8.5‰ for all calcites formed at surface-normalized growth rate greater than $10^{-5.5} \text{ mol m}^{-2} \text{ s}^{-1}$. This is further supported by the isotopic fractionation measured in the experimental work by Day et al. (2021) where calcite growth occurred at a rate of $\sim 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ (Fig. 2B). In addition, the changes in $\Delta^7\text{Li}_{\text{calcite-fluid}}$ induced by increased pH from 6.3 to 9.5 are on the order of $\sim 3\text{‰}$ although the surface-normalized growth rate is similar in these runs. These findings suggest that the direct use of Li in natural samples may not be applicable without additional calibrations related to the control of growth kinetics on Li isotope fractionation at pH conditions different from those in our experiments of 8.25 ± 0.15 . In addition, it must to be considered that the chemical composition of the growth solution may exert significant controls on Li isotope composition in natural samples. For example, the presence of ions such as Mg^{2+} and SO_4^{2-} that are present in high concentrations in seawater can, to some extent, alter the unit cell parameters of calcite (Goetschl et al., 2019). Albeit minor, these volumetric changes of cell parameter can likely affect both the elemental and the isotopic composition of small ions such as Li because these commonly are placed in the interstitial space of the solid phase. Similarly,

the isotopic composition of adsorbed species in calcite is affected by background electrolyte concentration, as recently shown for B sorption on calcite (Saldi et al., 2018).

The necessity for additional work constraining the mechanisms controlling Li isotope composition in calcite is further evident when considering previous experimental work. For example, Marriott et al. (2004a) reported $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values of -8.5‰ for experiments conducted at pH of 6.9–7.1 and calcite formation from a $\text{NaHCO}_3\text{--CaCl}_2$ solution, whereas Marriott et al. (2004b) reported $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values of -2.6‰ for calcite formation from a modified seawater solution. In these two studies the reported $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values fall within the range measured or modelled using the TST-fit presented in this work, although details for growth rate are not provided. More recently, Day et al. (2021) reported $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values of -9.0‰ at 25°C in experiments conducted at pH of 7.2 and from a diluted background electrolyte solution. Although the pH difference of these runs compared to those of this study that are displayed in Fig. 2 is ~ 1 unit, they fit well within the range of the largest fractionation predicted by the TST-fit (Fig. 2B). If this kinetic effect holds true, i.e., a similar kinetic Li isotope fractionation factor can be applied to the formation of the samples by Day et al. (2021), it indicates that our findings strongly contradict the conclusions drawn by these authors, that Li isotopes in natural calcites exhibit low sensitivity to growth rate. Indeed, in our study mineral growth rate and S_{calcite} are positively correlated (see ESM Fig. 1 in Fuger et al., 2019) and exert control on $\Delta^7\text{Li}_{\text{calcite-fluid}}$ values (Fig. 2). Thus, S_{calcite} is expected to affect the $\delta^7\text{Li}_{\text{calcite}}$ of natural calcite during its formation from aqueous fluids. In contrast in Day et al. (2021) calcite formation from fluids with different S_{calcite} yield identical growth rates. This lack of correlation between S_{calcite} and mineral growth rate is a rather uncommon feature, that likely only occurs during mineral growth from a thin water film e.g. in speleothems (Day and Henderson, 2013; Lindeman et al., 2022) and cannot be generalized to the growth of other natural calcites.

In biogenic samples, commonly of marine origin, the controls of Li chemical and isotopic composition in calcite are also somewhat convoluted. For example, in brachiopods, $\delta^7\text{Li}$ does not exhibit a clear relationship with the seawater pH between 7.6 and 8.2 (Washington et al., 2020). Moreover, the Li isotope compositions are similar between the shell layers (Washington

et al., 2020; Gaspers et al., 2021), whereas the apparent D_{Li}^* is distinct (Rollion-Bard et al., 2019). As shown here and by Fuger et al. (2019), precipitation rates have an effect on both the Li isotope composition and D_{Li}^* and the same holds true for pH. Thus, it appears difficult to discuss the variation in D_{Li}^* values solely as an effect of varying precipitation rate. This observation suggests that in the case of brachiopods, the precipitation pathway should be considered.

A similar situation may arise for foraminifera, that commonly are used for paleo-pH reconstructions and whose Li isotope composition has been proposed as complementary tool for estimating this parameter (Roberts et al., 2018). Note that at present, paleo-pH estimates routinely utilize B isotopes (e.g., Jurikov et al., 2020), but the integrity of B isotopes as a proxy has been recently questioned based on experimental work (e.g., Mavromatis et al., 2015; Noireaux et al., 2015; Uchikawa et al., 2015; 2017; Farmer et al., 2019). Earlier studies on foraminifera shells as well as on shallow- and deep-sea corals demonstrated no dependence of Li isotope on the pH (e.g., Rollion-Bard et al., 2009; Vigier et al., 2015), whereas recently Roberts et al. (2018) showed an anti-correlation between $\delta^7Li_{calcite}$ and pH. Whether this effect is originating from species-specific biological effects has to be further explored, but the observed variation on δ^7Li among different foraminifera species, and in general among marine calcifiers, may be associated with crystallization via an amorphous precursor. At present, the mechanisms controlling trace metal chemical composition and isotope fractionation during calcite formation via an amorphous calcium carbonate (ACC) precursor are under scientific scrutiny (e.g., Purgstaller et al., 2016; Littlewood et al., 2017; Dietzel et al., 2020; Goetschl et al., 2021). Mavromatis et al., (2017b) have shown that during calcite formation via ACC formation and subsequent transformation, the amorphous phase exhibits a smaller extent of Mg isotope fractionation compared to the crystalline calcite product, an observation consistent with that made for O (Dietzel et al., 2020), B (Mavromatis et al., 2021) and Ca (Gussone et al., 2011). This may also be valid for Li, although the existing differences in the incorporation sites of Mg or Ca compared to Li in the solid phase have to be considered (e.g., Dellinger et al., 2018).

Finally, although the direct comparison of Li elemental and isotopic compositions produced during the inorganic experiments conducted in this study with natural calcite of biogenic origin may not be straightforward, there is an interesting finding suggesting the use of Li as proxy tool. Combining the findings of this study with the results of Fuger et al. (2019) on Li elemental distribution in the same set of samples, we postulate that Li distribution coefficients and Li isotope fractionation factors between calcite and aqueous fluid can be used as a potential tool to estimate the formation rate of natural calcite, with the aid of Eq (8). Indeed, the correlation between $\Delta^7\text{Li}_{\text{calcite-fluid}}$ and $D_{\text{Li}^+}^*$ values that is described using Eq (8) and plotted in Fig. 4 is independent of the precipitation rate of calcite and forming pH for all the samples analyzed in this study. We attribute this feature to the same mechanisms controlling Li concentration and isotopic composition in the solid; likely through the initial formation of surface complexes that later incorporate in the solid. This dependence suggests that at a defined $(\text{Li}/\text{Ca})_{\text{aq}}$, the Li concentration in the precipitated calcite mirrors the $\Delta^7\text{Li}_{\text{calcite-fluid}}$ value. In similar terms, for a known $(\text{Li}/\text{Ca})_{\text{aq}}$ the $\delta^7\text{Li}_{\text{fluid}}$ of a reactive solution during calcite formation may be estimated from the measured Li concentration and $\delta^7\text{Li}$ of the precipitated calcite if both these parameters are known or can be reasonably estimated. If calibrated properly, this approach might be useful in marine settings, because the rather conservative residence time of Li^+ of about 1–1.5 Myr is reflected in less variable concentration of Li over time in oceans, compared to respective timescales of transient Li isotope changes in hundreds of kyr (e.g., Pogge von Strandmann et al., 2013; Day et al., 2021).

Overall, the results of our study indicate that Li isotopes may provide new insights into the formation conditions of natural calcite. However further investigation of Li isotope fractionation is required, including aspects like (i) fractionation throughout the formation and transformation of ACC; (ii) fractionation during the growth of biogenic calcite, and (iii) high-resolution spectroscopic studies in order to verify whether Li is incorporated with its hydration sphere or not, are highly encouraged.

5 CONCLUSIONS

The findings of this study demonstrate a significant Li isotope fractionation between calcite and the formation fluid, which is affected both by growth rate and pH. The observed Li isotope fractionation between calcite and reactive fluid can be better explained by the large kinetic isotope fractionation factor of $\alpha_f = 0.9912 \pm 0.0001$ that best fits the TST-derived fractionation for our measured data at pH 8.25 ± 0.15 . At increasing growth rates, preferential incorporation of ^6Li into the growing calcite is observed. This enrichment is associated with the desolvation of the $\text{Li}^+(\text{aq})$ ion that promotes the preferential attachment of ^6Li onto the calcite surface at elevated growth rates. In addition, the new results suggest that in the pH range between 6.3 and 9.5 for calcite formed under near equilibrium conditions, Li isotope fractionation increased from $-5.28 \pm 0.20 \text{ ‰}$ to $-1.78 \pm 0.23 \text{ ‰}$. This observation suggests that the Li isotope composition of the solid is not controlled only by the presence of LiHCO_3° in calcite that has been earlier argued in Fuger et al. (2019), but two or more Li-bearing species are present in this mineral phase. Overall, the results suggest that Li isotopes in calcite have the potential to be used as a proxy tool, however additional calibrations for the effect of growth rate, pH and solution composition are required.

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Table 1: Lithium isotope composition of reactive fluids, time of fluid sampling, calcite and reference materials analyzed in this study, together with pH, calcite growth rate and activity of HCO_3^- (aq) ion occurred in each run during mineral formation and estimated $D_{\text{Li}^+}^*$ values.

Experiment*	Time of sampling (min)	$\delta^7\text{Li}_{\text{fluid}}$ (‰)	2s.d.	$\delta^7\text{Li}_{\text{calcite}}$ (‰)	2s.d.	$\Delta^7\text{Li}_{\text{calcite-fluid}}$ (‰)	pH	$\log r_p$	$\log D_{\text{Li}^+}^*$	$\log a_{\text{HCO}_3^-}$
2_30	End of run	8.39	0.05	5.8	0.21	-2.77	8.27	-8.1	-4.3	-2.80
2_40	Initial reactor	8.36	0.22	5.87	0.18	-2.7	8.29	-8.0	-4.1	-2.82
2_40 (CGS)	Initial reactor	8.22	0.19				8.29	-8.0	-4.1	-2.82
2_70				6.06	0.06	-2.51	8.27	-7.7	-4.1	-2.83
2_90 (CGS)				5	0.25	-3.57	8.4	-7.6	-4.1	-2.83
2_100 (CGS)				4.69	0.52	-3.88	8.25	-7.5	-3.5	-2.86
3_40				5.52	0.44	-3.05	8.33	-7.8	-4	-2.85
3_50	8580	8.5	0.12	5.23	0.16	-3.34	8.17	-7.6	-3.9	-2.90
3_60				4.57	0.28	-4.00	8.30	-7.5	-3.9	-2.86
3_70 (CGS)				4.67	0.38	-3.9	8.28	-7.4	-3.7	-2.88
5_50				5.06	0.19	-3.51	8.07	-7.4	-3.3	-2.78
5_60				4.94	0.09	-3.63	8.13	-7.3	-3.3	-2.81
5_60 (CGS)				4.59	0.17	-3.98		-7.3	-3.3	-2.81
5_80	7355	8.59	0.33	4.3	0.2	-4.27	8.09	-7.2	-3.3	-2.79
5_80 (CGS)	7355	8.59	0.18	4.06	0.25	-4.51	8.09	-7.2	-3.3	-2.79
7_25	8775	8.65	0.15				9.59	-8.1	-4.8	-3.25
7_25 (CGS)				6.31	0.32	-2.26	9.59	-8.1	-4.8	-3.25
7_50 (CGS)				6.79	0.28	-1.78	9.43	-7.8	-4.6	-3.14
7_100 (CGS)				6.71	0.17	-1.86	9.54	-7.5	-4.7	-3.25
12_70	8605	8.59	0.06	3.47	0.18	-5.10	6.34	-7.7	-3.0	-1.88
12_80				4.06	0.27	-4.51	6.31	-7.7	-3.0	-1.87
12_100				3.29	0.31	-5.28	6.31	-7.6	-2.9	-1.85
13_60	6865	8.72	0.11	5.66	0.25	-2.91	7.41	-7.8	-3.3	-2.44
13_60				5.21	0.29	-3.36	7.41	-7.8	-3.3	-2.44
13_70				5.75	0.11	-2.82	7.49	-7.7	-3.3	-2.47
Li stock solution		8.67	0.16							
NASS-6		31.51	0.18							
NASS-6 (CGS)		30.94	0.12							
IAPSO (CGS)		31.00	0.12							

* CGS denotes analyses of samples in Czech Geological Survey.