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# The reaction kinetics and Sn isotope fractionation of Sn(IV) chloride hydrolysis

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A R T I C L E I N F O	A B S T R A C T
Keywords: Hydrolysis Cassiterite Sn isotopes Kinetics Activation energy Sn(IV) chloride	Hydrolysis of Sn is a pivotal step during the precipitation of cassiterite, the primary Sn-bearing mineral and thermodynamically stable Sn-oxide on Earth's surface. In this contribution, we investigated the reaction kinetics of Sn(IV) chloride hydrolysis by systematic experiments at temperatures of 6.4 °C to 28.6 °C. Experimental results show that the hydrolysis reactions of Sn(IV) chloride follow a first-order kinetics model, with rate constants $(0.12 \text{ h}^{-1} \text{ to } 5.5 \text{ h}^{-1})$ strongly controlled by temperature. Based on the obtained reaction constants at different temperatures and the Arrhenius equation, the activation energy of the Sn(IV) chloride hydrolysis reaction is calculated to be $26.05 \pm 2.25$ kcal/mol, indicating a surface-controlled reaction mechanism. Additionally, the Sn (IV) chloride hydrolysis rate increases with the ionic strength. No significant Sn isotope fractionation between acueous Sn(IV) and the solid hydrolysis product was observed during the Sn(IV) hydrolysis experiments in this

## 1. Introduction

Tin is one of the first metals used by humankind and a critical metal in modern society for its indispensable applications in high-tech industries and low-carbon economies (Lehmann, 2021; Mao et al., 2022; Tarselli, 2017; Zhao et al., 2021). Tin is almost exclusively extracted from cassiterite (SnO<sub>2</sub>) of hydrothermal deposits. The formation mechanisms of cassiterite can be diverse, however, they are invariably related to the hydrolysis of aqueous Sn ions. For example, Sn mineralization can be promoted by H<sup>+</sup>-consuming processes during greisenization (alteration of feldspars and biotite) and in a skarn (Heinrich, 1990; Schmidt, 2018). This is because Sn hydrolysis, a fundamental step of cassiterite precipitation, is an H<sup>+</sup> liberating reaction (Heinrich, 1990; Schmidt, 2018; Taylor and Wall, 1993), so consumption of H<sup>+</sup> can facilitate the Sn hydrolysis reactions, thereby promoting the precipitation of cassiterite (Korges et al., 2018). Mixing of magmatic-hydrothermal fluid with meteoric water has also been proposed as a mechanism to trigger tin mineralization (Cheng et al., 2012; Harlaux et al., 2020; Yao et al., 2014), during which the process of rapid dilution expedites Sn hydrolysis (Harlaux et al., 2021). Therefore, understanding the Sn hydrolysis process is crucial for deepening our understanding of tin mineralization.

It was thought that Sn is mainly transported as Sn(II) species in hydrothermal systems (Lehmann, 1982), however, recent studies increasingly recognized the role of aqueous Sn(IV) in cassiterite mineralization under acidic and oxidizing conditions (Schmidt, 2018; Schmidt et al., 2021; Sherman et al., 2000). The coexistence of Sn(IV) and Sn(II) species under hydrothermal conditions has been identified by the in situ Raman spectroscopic method (Chou et al., 2021). More recently, Wang et al. (2021) used theoretical calculation and modeling approaches to argue that aqueous Sn(IV) was the most important Sn redox state in hydrothermal fluids prior to cassiterite precipitation. Therefore, oxidation is not always necessary for cassiterite precipitation (Liu et al., 2023; Schmidt, 2018). Among the various ligands that could form stable complexes with Sn in aqueous solutions (Müller and Seward, 2001), chloride is the most important anion in mineralizing fluids and Sn-Cl complexes are the dominant Sn species (Goldmann, 2016a; Liu et al., 2023). Despite the extensive studies on the precipitation mechanisms of Sn ores (Cheng et al., 2019; Codeço et al., 2019; Harlaux et al., 2021; Liu et al., 2019, 2020), the kinetic and thermodynamic details of hydrolysis of Sn(IV) chloride, presumably the most important Sn species during cassiterite mineralization, remains little known.

study. The activation energy data and Sn isotope behavior associated with Sn(IV) chloride hydrolysis may be used to better understand the behavior of Sn during various mineralization and weathering processes.

Exploration of mineral deposits depends on the models of metal

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enrichment in the crust (Mei et al., 2022), especially the chemical state and rate of metal transport and precipitation. Knowledge of the reaction kinetics of Sn(IV) chloride hydrolysis during such processes is the prerequisite for a quantitative understanding of Sn behavior in various geochemical systems by numerical modeling (Rai et al., 2011; Séby et al., 2001). In addition, there is increasing evidence that Sn isotope compositions are highly variable in various cassiterite from different mineral deposits (Liu et al., 2021; Mason et al., 2020; She et al., 2023; Wang et al., 2019; Yao et al., 2018; Zhou et al., 2022). Quantification of Sn isotope fractionation during hydrolysis reaction is necessary for interpreting the Sn isotope data of cassiterite. The mineralogy of Sn hydrolysis products, the relevant reaction kinetics, and the Sn isotope fractionation factors of Sn(IV) hydrolysis reactions remain largely unknown. To bridge these knowledge gaps, hydrolysis experiments of Sn (IV) chlorides were carried out under different temperature and ionic strength conditions, and Sn isotope compositions of solutions from hydrolysis experiments were analyzed. The experimental results imply that hydrolysis is a rapid process that plays a critical role in the transport and deposition of Sn. We also found no resolvable Sn isotope fractionation during the hydrolysis process.

## 2. Experimental

Approximately 59 mg analytical grade salt of SnCl<sub>4</sub>·5H<sub>2</sub>O was dissolved with 40 mL deionized water in a 50-mL centrifuge tube to prepare a starting solution that contained ca. 500 ppm Sn. Free-drift hydrolysis experiments were conducted in 50 mL centrifuge tubes immersed in a precision thermostatic water bath. The water bath temperature can be verified by a mercury thermometer. After the desired temperature was reached and stabilized, the SnCl<sub>4</sub>·5H<sub>2</sub>O was put in contact with deionized water, which induced visible Sn precipitate after the onset of the experiment. A Mettler Toledo pH meter and a thermometer were used to measure the pH and temperature in situ. The pH meter was calibrated against standard buffer solutions of pH 4.01 and 7.00 with an error within 0.05 pH units. Every tube contained a floating PFA-coated magnetic stir bar to homogenize the solution prior to sampling. After a certain time interval in the hydrolysis experiment, 0.5 mL of the fluid was harvested from the 50 mL tube after the pH and temperature measurements. The fluid was centrifuged at 14000 r/min for 2 min to separate the aqueous solution from the precipitates. The supernatant after centrifugation was pipetted to a new beaker and diluted in 3.6 mL 6 N HCl; the precipitates were washed with deionized water, centrifuged again, then re-dissolved in 2 mL 6 N HCl. 400 µL of the dissolved samples were used for elemental analysis.

We also performed ionic strength experiments in which the NaCl concentration was adjusted for the solution at a defined temperature before the onset of each run. The variation of ionic strength was achieved by adding different amounts of NaCl into the tubes to make NaCl solutions with concentrations ranging from 0.001 M to 0.2 M. Repeat experiments of Sn(IV) chloride hydrolysis in water were performed with two different starting materials (Hyd A1-4 vs. Hyd B1: SnCl<sub>4</sub>·5H<sub>2</sub>O salts from two different suppliers) under ambient conditions for Sn isotope analysis. The hydrolysis of Sn(IV) chloride in 2% HNO<sub>3</sub> (Hyd B2) was also carried out for Sn isotope measurement for comparison. Only the aqueous solution after precipitation and centrifugation was dissolved and diluted for Sn isotope analysis. It should be noted that we did not measure pH and temperature to avoid any potential contamination for Sn isotope measurements.

Repeat experiments were performed to acquire sufficient precipitates for further characterization, and some of the wet precipitates were dried with a Scientz vacuum freeze dryer. Both wet and dry precipitates were further ripened with successive steps: heating at 150 °C on a hotplate for 58 h (referred to as the HT experiment hereafter) or oven-drying in a high-pressure bomb for 70 h and then freeze-drying (referred to as the HP experiment hereafter). Some freeze-dry products were put into the high-pressure bomb and then heated at 100 °C on a hotplate (referred to as the HTP experiment hereafter). In the high-pressure step, the hydrolysis products were calcined in an oven at 200  $^{\circ}$ C and then cooled to ambient temperature. The treated products were crushed for further characterization if necessary.

All analyses were conducted at the State Key Laboratory for Mineral Deposits Research, Nanjing University. Powder X-ray diffraction (XRD) analysis of bulk sample powders was performed on a Rigaku D/max Rapid II X-ray Diffractometer. Transmission electron microscope (TEM) analyses of samples were performed on a Tecnai G2 F20 S-Twin TEM. A field emission scanning electron microscope (FE-SEM, Carl Zeiss Supra55) was used to characterize the micromorphology of the obtained materials. The surface area of the reaction product was determined by the BET method using N<sub>2</sub> adsorption on a Micrometrics ASAP 2020 apparatus. Elemental concentration analysis of solutions was performed with a Skyray inductively coupled plasma optical emission spectrometer (ICP-OES) (She et al., 2020). Sn isotope analysis of solutions from the hydrolysis experiments was performed using a Nu 1700 Sapphire multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (She et al., 2023b). The detailed descriptions of analytical methods in this study can be found in Appendix A of Electronic Supplementary Information (ESI).

## 3. Results

## 3.1. Mineralogical characterizations of the precipitated phase

After a short setting time during the Sn(IV) chloride hydrolysis experiment, visible colloidal particles appeared in the solution. The particles agglomerated to form semi-transparent, white-cloudy precipitates. The initial precipitated phase in the experiments is poorly crystalline and hydrous. The XRD patterns of all products are compared with standard synthetic cassiterite (SnO<sub>2</sub>) (PDF 41-1445) and commercial Sn(OH)<sub>4</sub> (Fig. 1a and b). It is important to note that only one phase was identified in each sample. All XRD patterns exhibit indistinguishable major peaks, particularly common peaks at 2 theta assigned to the (110), (101), (211), and (112) planes of the rutile-type structure. Search-match for phase identification was performed. The products not treated with high pressure (HP and HTP experiments) likely comprise less well-developed SnO2 similar to Sn(OH)4 based on their identical pattern. These peaks were broad and of relatively low intensity, without minor peaks typical of synthetic cassiterite (PDF 41-1445), implying the presence of the poorly crystalline product. The minor peaks of cassiterite (d = 2.369, 1.322, 1.2147) appeared after the hydrolysis products were treated at 150 °C (Fig. 1b). Under high-pressure conditions (HP and HTP experiment), the products collected were identified as pure SnO<sub>2</sub>, with intense and narrow peaks indicating better crystallinity.

Bright-field TEM images reveal that the domains of freeze-dried hydrolysis aggregates without heating treatment were quadrilateral or irregular with diameters of several hundred nanometers (Fig. 2a). The TEM characters of the hydrolysis products are similar for experiments with or without NaCl (Fig. 2a; Figs. S1a and b). TEM image shows randomly oriented particles and some clusters without clear grain boundaries (Fig. 2b and c). The selected area electron diffraction (SAED) pattern typically exhibited polycrystalline diffraction rings (Fig. 2d) but in some rare cases discrete diffraction points (Fig. 2e). The polycrystalline diffraction rings and short-range order indicate that the nanophase was crystallized in its early stage. The lattice of short-range crystalline does not exhibit any preferred orientation. Lattice-fringe measurements yielded interplanar distances clustered around 3.31 Å (3.18–3.48 Å), close to 3.35 Å, corresponding to the (110) plane of  $SnO_2$ . It coincides with the fact that cassiterite commonly occurs as prisms with (110) planes. An interplanar distance of about 2.67 Å is also seen, close to 2.64 Å ascribed to the (101) surface of  $SnO_2$ . The measurement of several polycrystalline rings generates the d-spacing of 3.254-3.439 Å, 2.550–2.735 Å,1.755–1.797 Å, respectively, corresponding to the (110) (101) and (211) planes of SnO<sub>2</sub> (Fig. 2d). It should be noted that the



Fig. 1. The measured XRD pattern of a) primary hydrolysis product and b) hydrolysis product treated with high pressure or high temperature, in comparison with commercially bought  $Sn(OH)_4$  and standard  $SnO_2$  XRD pattern.



**Fig. 2.** TEM micrograph for freeze-drying hydrolysis product: a) bright-field image of the subhedral aggregated domain from hydrolysis experiment in water; b, c) high-resolution TEM of nanoparticles' lattice fringe, lattice plane family can be identified with the labeled d-spacing for hydrolysis product in water; d) selected area electron diffraction ring of polycrystalline from hydrolysis experiment in water; e) selected area electron diffraction of monocrystal from hydrolysis experiment in water; f) high-resolution TEM of nanoparticles' lattice fringe for hydrolysis experiment with 0.03 M NaCl; g) high-resolution TEM of nanoparticles' lattice fringe for hydrolysis experiment with 0.03 M NaCl; g) high-resolution TEM of nanoparticles' lattice fringe for hydrolysis experiment with 0.03 M NaCl; h) selected area electron diffraction ring of polycrystalline for hydrolysis experiment with 0.03 M NaCl.

generated Sn nanoparticles and their diffraction rings under various ionic strengths are identical to those produced without NaCl (Fig. S1; Fig. 2f, g, h).

Representative SEM images of hydrolysis products before and after different treatments (e.g., HT, HP, HTP) are shown in Fig. 3. The freezedried products had a lamella shape that was flattened in two directions and irregular in another direction (Fig. 3a and b). Upon heating at 150 °C, the products show prismatic features and sometimes display steps or kinks on the surfaces (Fig. 3c and d). Thermal treatment seems to be effective in producing crystalline particles. While under highpressure conditions, the wet products present a porous and conchoidal surface and are coherent with the brittle fracture of cassiterite (Fig. 3e and f). It can be concluded that the small pellet was connected and healed under such conditions since the original sheet structure remained (Fig. 3e). With further heating, aggregation of pellets could be observed at this stage (Fig. 3g), and the prismatic crystals also appeared (Fig. 3h). High pressure and temperature increase the size or crystallinity of the hydrolysis product.

The BET surface area of the freeze-dried product was 143.9 m<sup>2</sup>/g, and that of commercial Sn(OH)<sub>4</sub> was 56.1 m<sup>2</sup>/g (Fig. S2). Moreover, the BET surface area for wet and dry products under heating at 150 °C and those under high pressure were determined to be 207.8, 138.1, 74.9, and



**Fig. 3.** Representative SEM images of hydrolysis product in the experiments with or without ripening: a, b) flaky freeze-drying product; c) wet product treated at 150 °C; d) prismatic crystal synthesis after freeze-drying product treated at 150 °C; e, f) wet product treated with the high-pressure bomb and then dried; g, h) freeze-drying product treated at 100 °C.

86.9  $m^2/g$ , respectively. This is consistent with the SEM evidence of coalescence under high pressure since the surface area became smaller than that without treatment.

## 3.2. Chemical characterization of reactive fluids

Temporal changes in pH and Sn concentrations of the aqueous solutions in the Sn hydrolysis experiments are tabulated in Table S1 and Table S2 and summarized in Fig. 4 and Fig. S3. The solutions' pH ranged from 1.74 to 1.91 for the temperature series experiments (Fig. S3) and 1.59–1.86 for the solution of ionic strength experiments. There is no notable change in the pH over time, but nearly all experiments had a drastic pH drop at the onset of the experiment from the near-neutral pH, which oscillated to a steady state in the end (Fig. S3). The patterns of pH evolution were temperature-independent and were similar in all experiments. Such results confirm the generation of  $\mathrm{H}^+$  through hydrolysis reaction during Sn precipitation.

During the hydrolysis experiments, the Sn content in the remaining aqueous solution decreased significantly with time. With an initial concentration of ~500 ppm, the precipitation of Sn after 6.87 h led to about 50% Sn(IV) loss for a temperature of 14.0 °C (Table S1). At the end of each experiment, the Sn concentration approached zero (detection limit of ICP-OES for Sn: 0.04 ppm), indicating nearly complete removal of Sn from the aqueous solution. Hydrolysis experiments at different temperatures exhibited similar trends of temporal evolution for Sn concentrations. The rate of Sn hydrolysis, reflected by the rate of decrease in Sn concentration of the aqueous solution, is strongly dependent on temperature (Fig. 4). For the variable temperature experiments, the time for a 90% of Sn(IV) loss ranged from 36.7 h at 6.4 °C to 0.35 h at 28.6 °C (Table S2).



Fig. 4. Temporal evolution of Sn concentration during the hydrolysis experiments at the indicated temperature.

Meanwhile, the duration for the Sn precipitation is shorter for experiments performed with NaCl under similar conditions. The speed of the hydrolysis reaction increased with increasing NaCl concentrations (Table S3). Specifically, the time for hydrolysis of 90% aqueous Sn(IV) chloride decreased from 5.9 h in 0.001 M NaCl solution to less than 0.02 h in 0.2 M NaCl solution at ~14.0 °C.

#### 3.3. Sn isotope results

The  $\delta^{122/118}Sn$  value of the residual aqueous phase of all repeated hydrolysis experiments exhibits reproducible trends (Fig. 5). The starting Sn(IV) chloride material has a  $\delta^{122/118}Sn$  composition of 0.09  $\pm$  0.03‰ (2SD, N = 3) and the  $\delta^{122/118}Sn$  range from  $-0.02\pm0.03\%$  (2SD, N = 2) to 0.15  $\pm$  0.04‰ (2SD, N = 2) for aqueous solutions of four repeated Hyd A experiments (Hyd A1-4). The  $\delta^{122/118}Sn$  composition for the Hyd B series starting material is  $-0.01\pm0.04\%$  (2SD, N = 3). The  $\delta^{122/118}Sn$  varies from  $-0.06\pm0.08\%$  (2SD, N = 2) to  $0.09\pm0.07\%$  (2SD, N = 3) for Hyd B1 experiment. Furthermore, the  $\delta^{122/118}Sn$  values of the solution for hydrolysis in 2% HNO<sub>3</sub> were also measured, which vary from  $-0.08\pm0.05\%$  (2SD, N = 3) to  $0.04\pm0.05\%$  (2SD, N = 3) for Hyd B2 experiment (Table 1).

## 4. Discussions

## 4.1. Kinetics of Sn hydrolysis in water

Knowledge of the chemical reaction process is a prerequisite for understanding the kinetics and thermodynamics of hydrolysis. The predominant aqueous species of Sn are  $SnCl_4(H_2O)_2$  and  $SnCl_6^{2-}$  according to quantum mechanical calculation and Raman spectroscopic observation (Schmidt, 2018; She et al., 2020). These aqueous species are stable under acid conditions but hydrolyze readily in neutral fluids. This is consistent with the fact that cassiterite solubility increases with increasing amounts of HCl (Liu et al., 2023; Zhao et al., 2021). The hydrolysis reaction equations are likely as follows:

$$SnCl_4(H_2O)_2 + 2H_2O = Sn(OH)_4 \text{ or } SnO_2 \cdot 2H_2O + 4HCl$$
  
 $SnCl_6^{2-} + H_2O = Sn(OH)_4 \text{ or } SnO_2 \cdot 2H_2O + 4H^+ + 6Cl^-$ 

The kinetics of mineral precipitation and dissolution have brought increasing attention yet remain a poorly understood topic (Jiang and Tosca, 2020; Oelkers et al., 2019; Schott et al., 2009). The reaction order can be determined by fitting the data to various rate equations (Poulton, 2003). The regression was performed for temperature series experiments (Fig. 6) via the equation: ln(1/C) = k\*t + b, where C is the concentration of aqueous Sn, k is the reaction rate constant, t is the reaction



Fig. 5. Evolution of Sn isotope compositions of the aqueous solution versus their respective proportions during hydrolysis experiments with two different starting materials: (a) Hyd A and (b) Hyd B. The stars denote the Sn isotopic composition of respective starting materials Hyd A and Hyd B. Hyd A1 – A4 represent the Sn isotope compositions of residual solutions after repeated hydrolysis experiments in MQ water. Hyd B1 and B2 denote the Sn isotope results of solutions after hydrolysis in MQ water and 2% HNO<sub>3</sub>, respectively. The shaded boxes indicate the external reproducibility. The error bars (2SD) are based on replicate analyses.

time, and b is a constant. The plots of ln(1/concentration) versus time increase linearly during the experiments (Fig. 6), implying first-order kinetics. The slopes of the corresponding data are taken as the apparent rate constants. As shown in Fig. 6, the rate constants increase from 0.12 h<sup>-1</sup> at 6.4 °C to 5.5 h<sup>-1</sup> at 28.6 °C. The rate constant equals 0.293 h<sup>-1</sup> for the experiment of 14.0 °C, consistent with the replicate experiment (0.291 h<sup>-1</sup>) (Fig. S4), which confirmed the validity and reproducibility of the kinetic rate constant.

According to the transition state theory, a chemical equilibrium exists between reactants and activated transition state complexes (White, 2013), and the potential energy barrier must be overcome to form the reaction product. Sparse thermodynamic data for Sn complexes and hydrolysis reactions had been reported (Jackson and Helgeson, 1985; Kopeikin, 2017; Séby et al., 2001), but no study included activation energy. Assuming that the measured rate is equal to the kinetic constant (De Giudici et al., 2005), the variation of the hydrolysis rate constant as Table 1

 $\delta^{122/118}Sn_{3161a}$  values for the hydrolysis experiments with two different starting materials, Hyd A and Hyd B.

Experiments	Hydrolysis media	Sample	Sn proportion	$\delta^{122/}_{^{118}Sn_{3161a}}$	2sd	N
Hyd A1	MQ Water	Hyd A starting	1.00	0.09	0.03	3
		material				
		11-31	0.95	0.04	0.03	2
		11-6l	0.86	-0.02	0.03	2
		11-101	0.72	0.11	0.04	2
		11-13	0.38	0.10	0.04	2
		11-201	0.06	0.07	0.01	з
Hyd A2	MQ Water	12-3l	0.99			3
		12-8l	0.82	0.06	0.03	3
		12-12l	0.59	0.10	0.04	3
		12–171	0.09	0.06	0.04	3
Hyd A3	MQ Water	14-21	0.99	0.09	0.04	3
		14-6l	0.83	0.05	0.00	2
		14-101	0.54	0.00	0.05	3
		14-161	0.19	0.03	0.08	3
		14–211	0.10	0.03	0.08	3
Hyd A4	MQ Water	15-31	0.97	0.10	0.08	3
-		15-71	0.80	0.03	0.05	2
		15-11	0.68	0.07	0.02	2
		15-151	0.38	0.03	0.03	3
		15-201	0.16	0.15	0.04	2
		13-241	0.08	0.03	0.08	3
Hyd B1	MQ Water	Hyd B	1.00	-0.01	0.04	3
		starting				
		material	0.00	0.01	0.00	
		5-11	0.93	-0.01	0.03	3
		5-21 5-31	0.92	-0.01	0.00	3
		5-41	0.87	-0.01	0.02	2
		5-51	0.87	-0.03	0.07	3
		5–61	0.84	0.04	0.08	3
		5–71	0.83	-0.01	0.08	3
		5-81	0.80	-0.01	0.07	3
		5-101 5-111	0.74	-0.02 -0.06	0.03	2
		5-121	0.57	0.05	0.08	2
		5–131	0.48	0.03	0.00	2
		5–14l	0.37	0.01	0.02	3
		5–151	0.26	-0.01	0.03	3
		5-161	0.21	-0.02	0.09	3
		5–171 5–181	0.09	0.09	0.07	3
Hyd B2	2% HNO <sub>3</sub>	6–11 6 21	0.96	-0.06	0.04	3
		6-31	0.95	-0.04	0.05	3
		6-41	0.96	-0.05	0.01	2
		6–51	0.95	0.01	0.09	3
		6–61	0.96	0.04	0.03	2
		6–71	0.95	0.01	0.03	3
		6-81	0.94	-0.06	0.06	2
		6-101 6-111	0.92	-0.03 0.01	0.01	2
		6-121	0.83	-0.01	0.05	2
		6–131	0.78	-0.02	0.06	3
		6–14l	0.71	0.04	0.05	3
		6–151	0.57	0.02	0.00	2
		6–161	0.45	0.03	0.05	3
		6-17l	0.33	0.02	0.03	3
		6-191	0.20	-0.08	0.05	3
		6-201	0.17	-0.05	0.03	2
				-	-	



Fig. 6. Logarithmic plot of the reciprocal Sn concentration versus elapsed time of temperature series experiments. Rate constants can be derived from the slope of dashed lines with the linear least-squares fit.



**Fig. 7.** a) The Sn precipitation rate constant (k) as a function of the temperature; b) Arrhenius plot of logarithmic Sn precipitation rate constant (ln k) as a function of reciprocal temperature (1/T). A linear least-squares fit of the data yields a slope corresponding to an activation energy of  $26.04 \pm 2.20$  kcal/mol. Analytical uncertainty in the measurements is shown except for those smaller than the symbol size.

a function of temperature (Fig. 7a) can be described by the Arrhenius equation (Saldi et al., 2012; Zhu et al., 2019):  $k = A^*exp(-E_a/RT)$ , where k is the reaction rate constant, A represents the Arrhenius pre-exponential factor,  $E_a$  denotes activation energy, R stands for the gas constant, and T refers to the absolute temperature (Table 2). An assumption for calculating activation energy is that all experiments' pre-exponential factor A stays the same (Metz and Ganor, 2001). The precipitation rate constant normalized to the BET surface area of the precipitate was used to calculate the activation energy of the Sn hydrolysis reaction. The slope yielded an activation energy of 26.05  $\pm$  2.25 kcal/mol (Fig. 7b).

The activation energy can be linked to the reaction mechanism of the hydrolysis process (Lasaga, 1984; Petrou and Terzidaki, 2014; Zhen-Wu et al., 2016). The mineral precipitation depends on two mechanisms: the surface reaction (adsorption, ion exchange, dissolution-precipitation) and diffusion of species to the surface, where the slower one is the rate-determining process (Davis and Hayes, 1987; Jiang and Tosca, 2020; Thanh et al., 2014). Reactions with activation energies lower than 5 kcal/mol are diffusion-controlled, indicating that the surface reaction rate is faster than the diffusion rate (Lasaga, 1984; Metz and Ganor, 2001). The surface-controlled reaction rates are commonly associated with activation energies around 10-20 kcal/mol (Ganor et al., 1995; Lasaga, 1984; Poulton, 2003). Precipitation experiments are often surface-controlled (Christoffersen and Christoffersen, 2003). In this study, the higher apparent activation energy ( $26.05 \pm 2.25 \text{ kcal/mol}$ ) signifies that the rate-determining step of the hydrolysis reaction is likely surface-controlled precipitation.

#### 4.2. Effect of ionic strength

Cassiterite is known to form in natural fluids at a range of salinities. Hydrothermal fluids are complex electrolyte solutions in which NaCl is the dominant component (Seward et al., 2014). In this study, we explored the influence of ionic strength on the rate constant by performing Sn hydrolysis experiments in various NaCl-bearing solutions. The rate constants increased from 0.41  $h^{-1}$  for 0.001 M NaCl to 0.84  $h^{-1}$ for 0.005 M NaCl of first-order kinetics (Fig. 8) and from 0.006  $\rm ppm^{-1}$   $\rm h^{-1}$  in 0.01 M NaCl to 1.8  $\rm ppm^{-1}$   $\rm h^{-1}$  in 0.2 M NaCl of second-order kinetics (Table S3), respectively. NaCl can help break hydrogen bonds between water molecules and change the structure and dynamics of water (Bouazizi et al., 2008; Hu et al., 2014; Huang et al., 2012; Sun, 2012). The enhanced reaction rate of Sn hydrolysis in high NaCl solutions can be due to the increased dissociation constant of water and increased production rate of OH, which facilitates a higher production rate of Sn(OH)<sub>4</sub>. Dipole interaction is also a possible explanation for the observed alteration in reaction rate since ionic strength can affect dipole interaction (Van Leeuwen, 1983). For NaCl-rich reaction, the involvement of concentrated Cl<sup>-</sup> and its interaction with aqueous Sn species prior to hydrolysis might be related to the change of reaction order.

Different ionic strengths could lead to different complex styles (i.e., outer-sphere and inner-sphere) (Mo et al., 2021). The ionic strength is related to the concentration of all ions present in the solution:

#### Table 2

Values of logarithmic rate constants (normalized by BET surface area,  $mol/m^2/s$ ) obtained from the regression of concentration data at the indicated temperatures.

temperature (°C)	lnk	ln(k) error
6.35	-20.06	0.03
12.91	-19.33	0.04
14.00	-19.16	0.08
17.70	-18.55	0.05
24.69	-17.08	0.05
28.63	-16.23	0.11

$$\mathbf{I} = \frac{1}{2} \sum Z_i^2 M_i,$$

where I is the ionic strength,  $Z_i$  and  $M_i$  are the valence and the concentration of the ith ion, respectively (García-García et al., 2007). Several models are available to decipher the activity coefficients with different realms of validity: The debye-Huckel model (I <  $10^{-2.3}$  M), Extended Debye-Huckel equation (I < 0.1 M), Davis equation (I < 0.5 M) (Kornicker and Morse, 1991). The Debye-Huckel theory predicts that the logarithm of the rate constant correlates with the square root of ionic strength (Lasaga, 1981), which can be seen in Fig. S5. A significant contribution to the complex behavior for higher and lower ionic strength may arise from the complicated species of Sn in the solution, which cannot be resolved in this study and awaits further work.

#### 4.3. Sn isotope fractionation during hydrolysis

The Sn isotope ratio in the solution represents the average dissolved Sn up to the sampling time. Although no published data on Sn(OH)<sub>4</sub> bond strength exists, an analogy can be made based on aqueous stannic solutions. The Sn–Cl bond (2.44-2.48 Å) is longer than the Sn–O bond (2.18–2.22 Å) in an aqueous solution (She et al., 2020), which will enrich heavier Sn isotopes in the Sn–O bond under isotope equilibrium (Schauble, 2004). The lack of resolvable Sn isotope variation during hydrolysis reactions (Fig. 5) thus reflects more kinetic processes rather than equilibrium isotope fractionation during the Sn(IV) chloride hydrolysis experiments in our study.

As demonstrated in Fig. 9, we propose that the hydrolysis process entails several successive steps: Sn(IV) hydrolysis to form six-coordinate aqueous species  $Sn(OH)_6^{2-}$ , transformation to four-coordinate  $Sn(OH)_4$ nanoparticle, and subsequent formation of colloidal precipitates (SnO<sub>2</sub> precursor). The dramatic pH decrease underlines the fast transformation of Sn(IV) chloride to  $Sn(OH)_6^{2-}$ . The dehydration of reactants is often the rate-controlling step during the crystallization process (Nancollas and Purdie, 1964). It could also take time to transform six-coordinate Sn species to Sn(OH)<sub>4</sub> by dehydration. Because the surface OH groups and H<sub>2</sub>O molecules in hydrated species could have a similar bonding effect (Nakada et al., 2017), substituting solvated Sn ions with the subsequent dehvdrated product may not yield a sufficient change in Sn-OH bond length. After the quick formation of  $Sn(OH)_6^{2-}$ , the dissolved Sn(IV) were depleted in our experiments, so the dehydration of the six-coordinated aqueous Sn species to Sn(OH)<sub>4</sub> may not involve sufficient isotope exchange between aqueous Sn(IV) and Sn(OH)<sub>4</sub>, which is consistent with the lack of Sn isotope fractionation in our experiments.

#### 4.4. Implications

#### 4.4.1. Hydrolysis in the weathering process

The dissolution of minerals is often controlled by the hydrolysis of metal-oxygen bonds on the surface site (Rosso and Rimstidt, 2000; Schott et al., 2009). Due to metal hydrolysis, significant amounts of colloidal metal elements have been observed in weathering profiles (Moravec et al., 2020). Tin sulfides such as stannite are important Sn-bearing minerals, and weathering of Sn sulfides generates various Sn hydroxides (Aleksandrov and Troneva, 2007), which finally transform into cassiterite (Haase et al., 2022). Tin also exists in Fe- or Ti-bearing minerals such as biotite, titanite, and magnetite by lattice substitution (Wang et al., 2013). Weathering of these minerals can release a large amount of Sn (Antunes et al., 2002). Sn released by chemical weathering can precipitate by hydrolysis reaction and adsorb by clay-rich mineral. Intense chemical weathering of sedimentary rocks on a stable continent could lead to the initial enrichment of Sn in the protoliths for further mineralization (Romer and Kroner, 2015, 2016).



Fig. 8. Plots of ln(1/Sn concentration) or (1/Sn concentration) versus elapsed time for hydrolysis experiments under various ionic strengths.



Fig. 9. The proposed reaction route of our hydrolysis experiments and subsequent transformation processes.

## 4.4.2. From Sn nanoparticles to cassiterite

Nanoparticles are defined as those with one or more dimensions smaller than 100 nm since, within the nanoscale range, mineral properties may begin to deviate from those of a bulk mineral (Hochella et al., 2008; Waychunas et al., 2005). As particles get smaller through the nano range of sizes, their solubilities increase exponentially (Hochella et al., 2008), contributing to efficient metal transport. We propose that the Sn nanoparticles from the hydrolysis reaction could form during fluid-rock interaction (weathering) and fluid mixing in hydrothermal vents. Sn-bearing nanoparticles, including those with lattice fringe d-spacing similar to  $SnO_2$ , have been found in mineral deposits and groundwaters (Hu et al., 2018; Lu et al., 2021; Yi et al., 2020).

Our experiments show that the hydrolysis product of Sn(IV) is the  $SnO_2$  precursor with structural similarity to  $SnO_2 \cdot 2H_2O$  or  $Sn(OH)_4$ . The gel-like  $SnO_2 \cdot 2H_2O$  could experience a composition of  $SnO_2 \cdot (2-X)H_2O$  (Supothina and De Guire, 2000) under heating and undergo complete

dehydration to cassiterite under hydrothermal pressure (Figs. 1 and 9). The rising temperature and pressure can facilitate the proton-based reorganization of the Sn–O framework (de Monredon et al., 2002). Under ripening, OH or lattice distortion could disappear gradually with increasing temperature (Diéguez et al., 2001). Consequently, the morphology and structure of the hydrolysis product after high-temperature or high-pressure treatment were altered (Figs. 1 and 3). The prismatic cassiterite was observed in this study (Fig. 3h), similar to cassiterite synthesized from carbonate solutions (Liu et al., 2020).

#### 4.4.3. Implications for interpretation of cassiterite Sn isotopes

Tin stable isotopes are increasingly used to constrain Sn-related magmatic-hydrothermal processes (Badullovich et al., 2017; Zhou et al., 2022). Sn isotope composition of primary cassiterite can vary in ore deposits and mineral scale (Liu et al., 2021; She et al., 2023; Zhou et al., 2022). Several mechanisms, including liquid-vapor separation, redox change, and fluid-rock interactions, have been proposed to explain these variabilities (She et al., 2020; Wang et al., 2019, 2021; Zhou et al., 2022). As shown in Fig. 9, hydrolysis is a key step in cassiterite precipitation from a Sn(IV) fluid. However, the isotopic effect of such a process has not been investigated in previous studies yet. The experiments in this study reveal the lack of Sn isotope fractionation from aqueous Sn(IV) to Sn(OH)<sub>4</sub> or SnO<sub>2</sub>·2H<sub>2</sub>O during low-temperature hydrolysis step of aqueous Sn(IV) is unlikely to account for the large Sn isotope variations of primary cassiterite from magmatic-hydrothermal systems.

Alluvial cassiterite is also the major source of tin (Goldmann, 2016b) and shows large Sn isotope variabilities (Haustein et al., 2010). Alluvial cassiterite can stem from primary cassiterite and terminal weathering of various Sn-bearing minerals. The Sn isotope variation of secondary cassiterite can result from several processes: Sn isotope variations of primary mineral, fractionation during mineral dissolution and precipitation, etc. Therefore, the Sn isotope variations of placer cassiterite likely predate the hydrolysis-dominated precipitation of secondary cassiterite.

#### 5. Conclusions

In this study, we performed systematic laboratory experiments to evaluate the reaction kinetics of Sn(IV) hydrolysis. The hydrolysis reaction of Sn(IV) chloride in water obeys the first-order reaction kinetics and generates a series of rate constants. The activation energy of 26.05 kcal/mol is deduced for our hydrolysis experiments, indicating a surface-controlled reaction mechanism. The reaction rate of Sn(IV) chloride hydrolysis increases with the ionic strength. In addition, the characterization of the reaction products shows that Sn nanoparticles can be produced by a hydrolysis reaction, which might enhance the transport of Sn in hydrothermal systems. Cassiterite can form from the nanoparticle under hydrothermal conditions. Our experimental rate and energy of the Sn hydrolysis process would bear on the Sn migration and precipitation research in weathering profiles and Sn mineralization. The solutions after hydrolysis exhibit indistinguishable Sn stable isotopic variations, which shows that Sn isotope fractionation during the Sn hydrolysis process is insignificant.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2023.105793.

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