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Diffusion of Sm-Nd in Scheelite and its Significance to Isotopic Dating and Tracing

ZHANG Dongliang[1, *], Ian M. COULSON[2], PENG Jiantang[1], LI Shijie[3] and WANG Guoqiang[4]

[1] *Key Laboratory of Metallogenic Prediction of Nonferrous Metals, Ministry of Education, School of Geosciences and Info-physics, Central South University, Changsha 410083, China*
[2] *Solid Earth Studies Laboratory, Department of Geology, University of Regina, Regina, Saskatchewan S4S 0A2, Canada*
[3] *Lunar and Planetary Science Research Center, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*
[4] *Xi'an Center of Geological Survey, CGS, Xi'an 710054, China*

Abstract: As the principal ore mineral in various tungsten (-gold) deposits, scheelite ($CaWO_4$) plays an important role in directly dating the timing of ore formation, and in tracing associated material sources through the study of its Sm-Nd geochronology and Nd isotopic characteristics. Since the retention of Sm-Nd systematics within scheelite is presently unconstrained, equivocal interpretations for isotopic data resulting from this method have occurred quite often in previous studies that apply these isotopic data. In order to better elucidate the closure of Sm-Nd in scheelite, the kinetics of Sm and Nd within this mineral lattice were investigated through calculation of diffusion constants presented herein. The following Arrhenius relations were obtained:

$$D_{Nd} = 4.00\exp(-438\ \text{kJ}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}$$
$$D_{Sm} = 1.85\exp(-427\ \text{kJ}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}$$

showing diffusion rate of Nd is near identical to Sm in scheelite when at the same temperature. However, compared to other rare earth elements (REEs), which have markedly different atomic radii to either Nd or Sm, these are shown to exhibit a great variation in diffusivities. The observed trends in our data are in excellent agreement with the diffusion characteristics of REEs in other tetragonal ABO_4 minerals, indicating that ionic radius is a key constraint to the diffusivity of REEs in the various crystal lattices. With this in mind, the same substitution mechanism and a very slight discrepancy in radii will allow us to infer that significant Sm/Nd diffusional fractionation in scheelite is unlikely to occur during most geological processes.

Based upon the diffusion data determined herein, Sm and Nd closure temperatures and retention times in scheelite are discussed in terms of diffusion dynamics. Those results suggest that closure temperatures for Sm-Nd within this mineral are relatively high in contrast to the temperature ranges of ore-formation responsible for scheelite-related deposits, and any later thermal environments. It is likely, therefore, that relevant isotopic information could be easily retained under most geological conditions, since initial crystallization of the scheelite. In addition, comparison of this mineral-element pair over a range of temperatures with some other common minerals used as geochronometers (e.g., zircon and apatite) indicates that Sm-Nd system has a slower diffusive rate in scheelite than for Sr in apatite or Ar in quartz, and only a little faster than for Pb in zircon. It should be noted, within most hydrothermal deposits where zircon has crystallized, its size is typically no more than 100 μm, whereas scheelite commonly occurs as macroscopic grains. For this reason, the larger dimensions of scheelite would provide a robust Sm-Nd system more able to resist perturbations, relating to any later thermal process. As such Sm-Nd investigations of scheelite are akin to U-Pb within zircon samples used in isotopic dating. These observations indicate that Sm-Nd age and isotopic information can provide reliable data in all but the most extreme case, especially when data are extracted from macroscopic grains of scheelite that are chosen to be "pristine" (i.e., free of surface alteration and/or fractures).

Key words: Sm-Nd system, diffusion, scheelite, closure temperature, isotopic dating

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1 Introduction

Scheelite, $CaWO_4$, may occur in a wide variety of ore deposits that includes those related to: skarns, aplite and pegmatite, metamorphic stratabound ore, and hydrothermal vein type (Brugger et al., 2000a; Zhang et al., 2022). Since trivalent REE can be incorporated into Ca-bearing minerals through substitution at Ca^{2+} structural sites in the mineral lattice (Zhong and Mucci, 1995; Ghaderi et al., 1999; Cherniak et al., 2001; Brugger et al., 2002; Dostal et al., 2009), scheelite commonly accommodates considerable amounts of Sm and Nd (Brugger et al., 1998,

* Corresponding author. E-mail: dlzh04@mails.ucas.ac.cn

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2008; Peng et al., 2003; Zhang et al., 2012a; Sciuba et al., 2020; Wang et al., 2021). Sm-Nd isochron dating method represents a very useful geochronologic tool for dating hydrothermal activities, whereby Nd is a most effective tracer to monitor the evolution of the mineralizing fluids (Fryer and Taylor, 1984; Liu et al., 2007; Dostal et al., 2009; Fisher et al., 2020). For such reasons, scheelite offers great utility with respect to geochronology and isotopic geochemistry, especially for those studies relating to tungsten (W) mineralization in complex polymetamorphic settings. Here ore mineralogy will provide more precise information than accessory minerals presumed to be co-genetic with ores or those relying on referred relationships (e.g., Bell et al., 1989; Eichhorn et al., 1997; Brugger et al., 2000a; Peng et al., 2003). Moreover, scheelite commonly occurs with native gold (Au) in many hydrothermal deposits, where the W abundance typically shows a positive correlation with Au concentration in ores (Ludden et al., 1984; Bell et al., 1989; Anglin et al., 1996; Ghaderi et al., 1999; Plotinskaya et al., 2018). Thus, its Sm-Nd age and Nd isotopic composition can be further used to determine the timing of Au precipitation, as well as, the origin of the mineralizing fluid responsible for the gold deposits (Anglin, 1990; Darbyshire et al., 1996; Oberthür et al., 2000; Voicu et al., 2000; Brugger et al., 2002; Peng et al., 2003; Roberts et al., 2006). Up to now, scheelite Sm-Nd dating has attracted much attention, and the timing of many important hydrothermal events have been successfully determined via this method (Anglin, 1990; Darbyshire et al., 1996; Eichhorn et al., 1997; Oberthür et al., 2000; Kempe et al., 2001; Peng et al., 2003; Roberts et al., 2006; Liu et al., 2007; Guo et al., 2016); however, this geochronometer has frequently failed in isotopic dating due to Sm-Nd isotopic data that presented non-linear trends (e.g., Oberthür et al., 2000; Peng and Frei, 2004; Peng et al., 2008) or where the linear regression result obviously differs from the actual timing of ore formation (e.g., Bell et al., 1989; Kent et al., 1995; Anglin et al., 1996). Such problems have led some to question this method's reliability. For example, several researchers (e.g., Kempe et al., 2001) consider that Sm-Nd isotope systematics within scheelite as comparatively sensitive to post-mineralization thermal events, such that even a slight disturbance may contribute significantly to isotopic data scattering in Sm-Nd diagrams, that would yield a false isochron or equivocal isotopic constraints (e.g., Corfu, 1993; Kent et al., 1995; Anglin et al., 1996; Frei et al., 1998).

Theoretically, one of the most important prerequisites in isotopic methodology is that a mineral of interest must remain closed for the isotope system since its initial crystallization (Giletti, 1974; Anglin et al., 1996). A great many studies reveal that the process of diffusion plays a key role in the distribution of trace elements within and between minerals of rocks exposed to thermal conditions for extended time periods (Dodson, 1973; Ganguly and Tirone, 1999; Chakraborty, 2006). During such thermal processes, trace elements and their isotopes contained within mineral phases can be redistributed. The degree of these perturbations is mainly dependent on the diffusion rate of the elemental species in the mineral of interest (Giletti, 1986; Cherniak and Watson, 1994; Ganguly et al., 1998). Hence, it is necessary to understand the kinetic behavior of Sm and Nd within the scheelite lattice in order to attain a greater insight into its reliability at various geological environments. In this study, we investigate Sm-Nd diffusion characteristics in scheelite, in attempts to elucidate the closure of Sm-Nd systematics in this mineral.

2 Diffusion Constants

The process of chemical diffusion in crystalline solids is considered to obey the following Arrhenius law of kinetics (Dodson, 1973):

$$D = D_0 \exp(-E/RT) \tag{1}$$

where D represents the diffusion coefficient at absolute temperature T, D_0 and E are the pre-exponential factor and activation energy, respectively, and R the gas constant. Since E and D_0 are independent of temperature and diffusant concentration, both are regarded to be diffusion constants. Thus, using this equation (1) it is possible to calculate D at any temperature from the given diffusion constants. Diffusion constants for an increasing number of species in a wide variety of minerals have been experimentally determined (e.g., Freer, 1981; Brady, 1995; Cherniak and Watson, 2011; and references therein).

Except for laboratory simulation, theoretical calculation and empirical prediction, based on the relationships between diffusion properties with crystal structure and thermodynamics, are the most effective methods to obtain diffusion constants. In such ways the diffusivity of O, Ar, H, Sr, Mg and Pb in various minerals have been well investigated according to corresponding models (Voltaggio, 1985; Fortier and Giletti, 1989; Zheng and Fu, 1998; Jaoul and Sautter, 1999; Zhao and Zheng, 2007; Zhang et al., 2011). By study of the correlation of experimental diffusion data with measurable crystal-chemical parameters, Zhang et al. (2012b) presented a method to calculate E (kJ/mol) and D_0 (cm^2/s) of REEs diffusion in different minerals, where REE^{3+} substitution for the lattice cations of 8-fold coordination, can be written as:

$$E = \frac{358.61V_A + 972.58V_B - 267.63V_C}{NV_1} - \frac{515.90V_A + 1109.97V_B - 361.03V_C}{NV_2} + 290.70 \tag{2}$$

$$\ln D_0 = \frac{30.94V_A + 100.04V_B - 24.78V_C}{NV_1} - \frac{37.07V_A + 95.65V_B - 27.41V_C}{NV_2} - 5.42 \tag{3}$$

Where V_A, V_B, respectively, represent the sum volumes ($Å^3$) of anions and cations in a unit-cell; V_C is the unit-cell volume ($Å^3$), and N is the number of molecule within a unit-cell; V_1 and V_2 are volumes ($Å^3$) of diffusing REE^{3+} and the substituted cation from the mineral lattice. Constants of rare earth elements diffusion in different

mineral lattices (substitute for 8-fold coordination site) under a dry, 1 atm condition, can be calculated according to the above equations and crystal chemical parameters of the associated ions and mineral cells. Shannon (1976) pointed out that crystal radii correspond more closely to the physical size of ions. Hence, the values of ionic radii in calculation of E and D_0 based on the model herein should use those given by Shannon (1976) for crystal radius.

Scheelite has a simple crystal structure with tetrahedral $[WO_4]^{2-}$ groups and irregular dodecahedral $[CaO_8]^{14-}$ groups (Brugger et al., 2000a), therefore, REEs in this mineral are incorporated into the site of 8-fold coordinated Ca^{2+} (Ghaderi et al., 1999). The associated crystal chemical parameters for the scheelite Sm-Nd pair are listed in Table 1. By calculating E and D_0 of the two diffusing species in scheelite, according to these crystal chemical parameters and the above equations, for Nd we obtain an activation energy of 438 kJ/mol and a pre-exponential factor of 4.00 cm^2/s ($\ln D_0 = 1.39$). For Sm these constants are 427 kJ/mol and 1.85 cm^2/s ($\ln D_0 = 0.62$), i.e., Arrhenius relations of the two rare earth elements are $D_{Nd} = 4.00\exp(-438\ kJ\cdot mol^{-1}/RT)\ cm^2/s$ and $D_{Sm} = 1.85\exp(-427\ kJ\cdot mol^{-1}/RT)\ cm^2/s$ (seeing Supp. Data for the detailed calculation).

Table 1 Crystal chemical data of REEs-scheelite diffusion system

Diffusing specie		Lattice cation		N	V_A	V_B	V_C
Ion	Radius	Ion	Radius				
$^8Nd^{3+}$	1.249 Å	$^8Ca^{2+}$	1.260 Å	4	121.70 $Å^3$	36.46 $Å^3$	312.60 $Å^3$
$^8Sm^{3+}$	1.219 Å						

Note: (a) The left superscript of the element symbol is the ionic coordination number in the scheelite structure, the right superscript is ionic valence; (b) cell dimensions of scheelite cited from Sleight (1972).

3 Diffusion of Sm-Nd in Scheelite

Arrhenius relations of Sm and Nd diffusion in scheelite are illustrated in Fig. 1. This figure shows that diffusivities between the two elements do not differ dramatically in scheelite over the investigated temperature range. This may be because Sm and Nd are quite similar in ionic radii (1.219 Å and 1.249 Å in eight-fold coordination, respectively; Shannon, 1976). To better understand the kinetics of REEs diffusion in this mineral, Yb (1.125 Å, 8-fold coordination), another rare earth element of a radius significantly different to that of Sm and Nd, was investigated by calculating its diffusion constants of E and D_0 in scheelite (386 kJ/mol and 0.09 cm^2/s, respectively). Figure 1 shows a comparison of their trends, and reflects a pronounced variation in diffusion coefficients from Yb^{3+} to Sm^{3+} and Nd^{3+}, and that the discrepancy will become larger when the temperature decreases. For example, at a temperature of 1000°C, the ratios of D_{Yb} with D_{Nd} is 3; while at 600°C, the value is >28. Namely, a variation of 10% in ionic radius (Δr) among these elements can lead to the rate for their diffusion in scheelite to increase or decrease at least several orders over the investigated temperature range.

Scheelite ($CaWO_4$) is structurally similar to zircon ($ZrSiO_4$) and xenotime (YPO_4), with all of these minerals

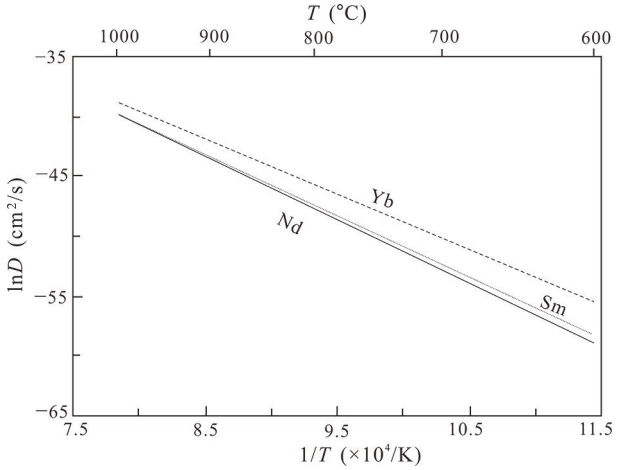


Fig. 1. Arrhenius plot for REEs diffusion in scheelite.

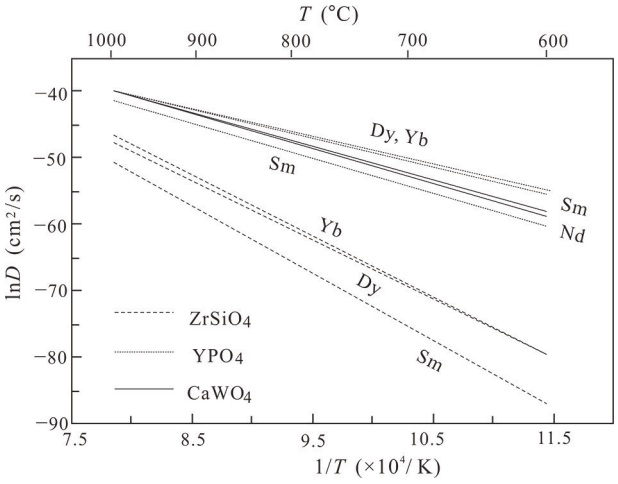


Fig. 2. Arrhenius plot for REEs diffusion in ABO_4 minerals.

being tetragonal compounds with structural formulas of ABO_4, and comprising dodecahedral $[AO_8]$ and tetrahedral $[BO_4]$ groups (Pan, 1993; Ni et al., 1995; Mi et al., 1996). Diffusivity for REEs in the three minerals are plotted in Fig. 2 as a function of temperature, with the diffusion data for zircon and xenotime taken from Cherniak et al. (1997a) and Cherniak (2006). By systematic comparison, it is evident that REEs diffusion in zircon is slower than that in scheelite and/or xenotime at the same temperatures. This difference maybe be attributed to the relative ionic radii of trivalent REEs and of the substituted cations within each of the minerals' lattices. In xenotime and scheelite, REE^{3+} are incorporated on the Y^{3+} and Ca^{2+} sites, respectively; whereas in the case of zircon, REE^{3+} will substitute on the lattice sites of Zr^{4+}. The differences in size between the lattice cation Zr^{4+} and the diffusing Sm^{3+} and Nd^{3+} in zircon are 0.24 Å and 0.27 Å, respectively; in contrast, the variations of Y^{3+} in xenotime and Ca^{2+} in scheelite to these $REEs^{3+}$ are between 0.01–0.09 Å. In view of the fact that diffusivities can be influenced by cationic size (Cherniak et al., 1997b, 2001; Van Orman et al., 2001), the considerably differences in radii is thought to result in REE^{3+} in substitution for Zr^{4+} in zircon to be more difficult than for

Y^{3+} and Ca^{2+} in corresponding minerals.

Besides exhibiting the pronounced differences among these ABO_4 typed minerals, REEs show a systematic increase in diffusivity with decreasing ionic radius in both zircon and xenotime (Fig. 2); this trend coincides with the observations from Sm, Nd and Yb diffusion in scheelite (Fig. 1), indicating that, in the same mineral lattice, variations of diffusion rates among the rare earth elements are strongly controlled by their ionic radii. Accordingly, Nd displays a similar diffusivity with Sm in scheelite that can be thought to reflect a very slight discrepancy in their ionic radii (1.219 vs. 1.249), with Δr of about 2.40%. In the scheelite lattice, therefore, diffusive fractionation on Sm/Nd is unlikely because the difference between Sm and Nd diffusivities is quiet small, and thus Nd diffusion data can be used directly as the representation of Sm-Nd system diffusion in scheelite. It should be made clear, however, that these diffusion data apply strictly to crystalline scheelite.

4 Geological Applications

Diffusion presents a fundamental mass transport process (Cherniak and Liang, 2007), and the relevant data are often used to understand isotope dating, cooling, geothermometry, and zoning structure in solid minerals (Zhang et al., 2006). In this section we will apply the diffusion data presented above to estimate whether scheelite precipitated from ore-formation fluids are likely to retain original Sm-Nd signatures under a thermal condition or potentially have an altered Sm-Nd chemical composition.

4.1 Closure temperature

The principle that a mineral remained as a closed system since initial crystallization is a basic precondition for isotopic dating and tracing (Giletti, 1974; Anglin et al., 1996). For an exact estimation of whether an apparent age corresponds to the crystal timing, or instead reflects the time the concentration of a specific element was effectively fixed and the mineral isolated from its surroundings, the low limit temperature at which the mineral could effectively close the species must be accurately determined. The low temperature limit at which an element in a given mineral effectively stops diffusive exchange with its surrounding medium is termed the closure temperature (T_C). The classical expression for closure temperature is from Dodson (1973) and is described as the following term:

$$T_C = \frac{E/R}{\ln\left(-\frac{ART_C^2 D_0/\alpha^2}{E(dT/dt)}\right)} \quad (4)$$

in which E and D_0 are diffusion constants from the Arrhenius relation, R is the gas constant, $-Dt/dt$ is the cooling rate, and α is the effective diffusion radius. A represents a geometric factor (for a sphere, A is equal to 55). The spherical geometric factor is used in this case because REEs diffusion does not appear to be strongly anisotropic in tetragonal ABO_4 type crystals; such as those in zircon and xenotime (Cherniak et al., 1997a; Cherniak, 2006). Since closure temperature varies with distance from the crystal surface (Dodson, 1986), T_C calculated using Eq. 4 are mean values. Cherniak (2003, 2006) pointed out that for a very narrow outermost layer, closure temperatures will not differ from the mean by more than a few tens of degrees, for cooling rates between 1–10 °C/Ma and grain sizes of up to a few millimeters (Cherniak and Watson, 2003; Cherniak, 2006).

Based on Dodson's equation and the diffusion constants determined in this study, we obtained Nd closure temperatures for scheelite as a function of effective diffusion radius with various cooling rates. Results of the calculations, shown in Fig. 3, indicate closure temperatures are 914°C, 976°C and 1045°C for "α" equal to 1 mm at the cooling rates of 1 °C/Ma, 10 °C/Ma and 100 °C/Ma, respectively; when "α" equal to 1 μm, they will be 641°C, 677°C and 717°C for the same cooling rates. These results suggest, although more rapid cooling will elevate closure temperatures, numerical values of Nd T_C will vary by no more than tens of degrees for an order of magnitude increase in cooling rate.

Furthermore, we can use the simplified expression above to make broad comparisons of retention about Sm-Nd in scheelite, with various mineral-element pairs which display an excellent closure. It is well known that zircon has fairly high retention for Pb under most environments, and apatite is also an ideal phase for closure of Sr than with other accessory minerals (e.g., Cherniak and Ryerson, 1993; Cherniak and Watson, 2000). Accordingly, closure temperatures for Nd in scheelite as well as those for Pb in zircon and Sr in apatite are plotted in Fig. 4, at the given cooling rates of 1 °C/Ma and 10 °C/Ma. The results indicate scheelite has comparatively high temperatures to close Nd in its lattice. Such as, for a cooling rate of 10 °C/Ma, scheelite grains of 10 μm effective radius would remain closed to Nd diffusional exchange well below the temperature of 760°C, and for 0.5 mm effective radius

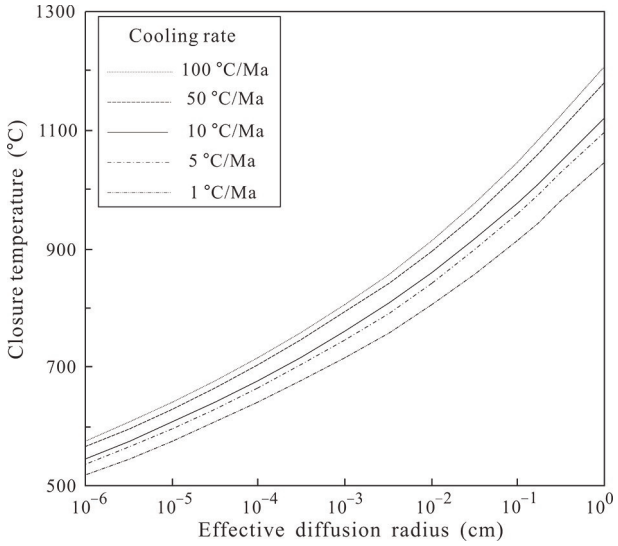


Fig. 3. Closure temperatures for Sm-Nd in scheelite as a function of effective diffusion radius for a series of cooling rates.
T_C of Sm-Nd is thought to be similar to Nd in scheelite.

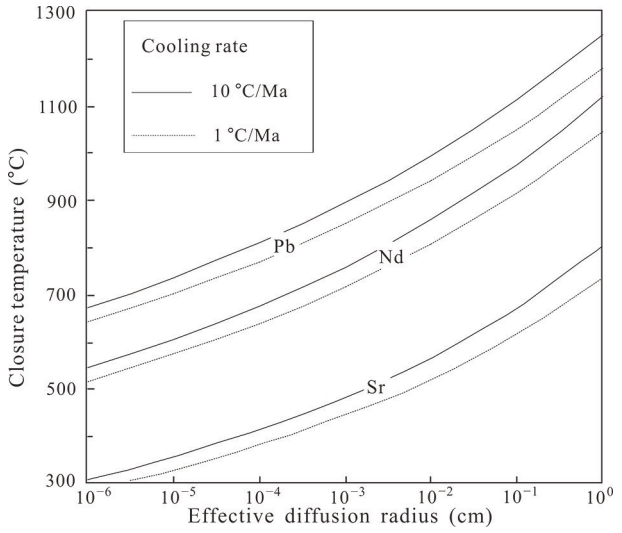


Fig. 4. Comparison of closure temperatures for Nd in scheelite with those for Pb in zircon and Sr in apatite, with cooling rates of 1 °C/Ma and 10 °C/Ma.

Sr and Pb closure temperatures were calculated with the diffusion data cited from studies by Cherniak and Watson (2000), and Cherniak and Ryerson (1993), respectively.

grains closure would be 938°C. While considering the same cooling rate, closure for Pb in 10 μm and 0.5 mm zircon grains would occur at temperatures of no more than 895°C and 1075°C, respectively; and for Sr in apatite, these values are 478°C and 633°C. Again, for effective diffusion radii of 10 μm and 0.5 mm, 1 °C/Ma cooling rate would result in closure temperatures of scheelite for Nd at about 717°C and 880°C, which are only about 130°C to 140°C lower than Pb in zircon, but 275°C to 300°C higher than Sr in apatite.

Before leaving this topic, it is worth pointing out that, according to previous studies, formation temperatures of scheelite in various types of ore deposit are commonly not very high. For example, in the Nanling metallogenic belt (in South China), microthermometric data from the Shizhuyuan tungsten-polymetallic deposit indicate that temperatures during the main ore-forming process focused on the range of 250°C to 350°C (Gong et al., 2004), and fluid inclusion studies on the Yaogangxian giant deposit constrain skarn type scheelite crystallization to temperatures of between 190°C and 300°C (Wang et al., 2007). At the Xuebaoding pegmatite-type W-Sn deposit (set in western China), homogenization temperatures (T_h) of fluid inclusions hosted in scheelite, as well as other hydrothermal minerals such as quartz, beryl and calcite from the mineralization phase, centralize on the range from 200 to 310°C (Cao et al., 2002) or from 275 to 300°C (Chen et al., 2002). Moreover, microthermometric studies indicate that scheelite from the Harare–Bindura–Shamva greenstone belt, Zimbabwe, formed over a temperature range of 250–380°C (Oberthür et al., 2000); while evidences from fluid inclusion data (O'Reilly et al., 1997) and isotope geothermometry (Gallaghe, 1989) show that the formation of scheelite-mineralized veins in southeast Ireland took place at temperature ranges of 360–530°C and 401–518°C, respectively. These results reveal that precipitation temperatures of native scheelites are mostly less than 550°C, obviously much lower than closure temperatures of Sm-Nd system in micron-grained scheelite during (slow) cooling processes. Thus, it is clear that, once crystallized, macroscopic grained scheelite will not experience a significant change in Sm-Nd composition under most geological environments.

4.2 Retention times

Under cooling conditions, retention of an element and its isotope in a given mineral grain can be evaluated through knowledge of closure temperature as discussed above. When a mineral is exposed to elevated temperatures for an extended period, however, trace elements and isotopic compositions between various mineral phase assemblages may lead to their redistribution among these minerals (Cherniak et al., 1990). In such a situation, relevant geochronologic and geochemical information may be perturbed or completely lost, dependent upon the duration of a particular heating event (Cherniak et al., 1991). In order to assess whether or not Sm-Nd isotope characteristics could significantly be affected in a particular grain or a region of a grain of scheelite when this undergoes various thermal events subsequent to initial crystallization, a simple model as proposed by Crank (1975) was applied.

The model considers the mineral crystals to be spheres of radius α with initial uniform concentration of diffusant C_1, and exposed to a medium with diffusant concentration C_0. When the dimensionless parameter Dt/α^2 (where D is the diffusion coefficient, t is the duration at elevated temperature) is <0.03, the center region of the spherical crystal can retain its original isotopic and trace-element signatures (Cherniak and Watson, 1992). When this parameter is >0.03, the concentration at the crystal core (α = 0) will be disturbed by the external medium and may no longer be equal to its initial value. The Sm-Nd diffusion data reported herein permit a determination of the degree that scheelite grains of more homogeneous composition will isotopically or chemically equilibrate with their external environment during heating, and could potentially alter the original Sm-Nd chemical signatures, noting that the model that follows applies strictly under conditions in which diffusion is the dominant mechanism of exchange.

A time vs. temperature plot of the curve satisfying the equality Dt/α^2 = 0.03 is shown in Fig. 5. Four sets of curves, each for a different value of α (1 mm, 0.1 mm, 10 μm and 1μm), are plotted for scheelite. These curves define the time-temperature limits for which Sm-Nd compositions in the scheelite grains will be retained. For times and temperatures below the curves, Sm-Nd isotopic ratios at crystal cores will remain unaffected, but they will be influenced by the concentration of Sm-Nd in the surrounding medium when conditions above the curves exist. These curves reveal that Sm-Nd isotope are much more likely to be retained in scheelite when it undergoes most thermal processes. For example, scheelite grains of 10 μm in effective radius will retain their Sm-Nd information when heated to 900°C for 7,200 years, or for 73 million years (Ma) when heated to 700°C. The temperature limits for scheelite crystals of radius

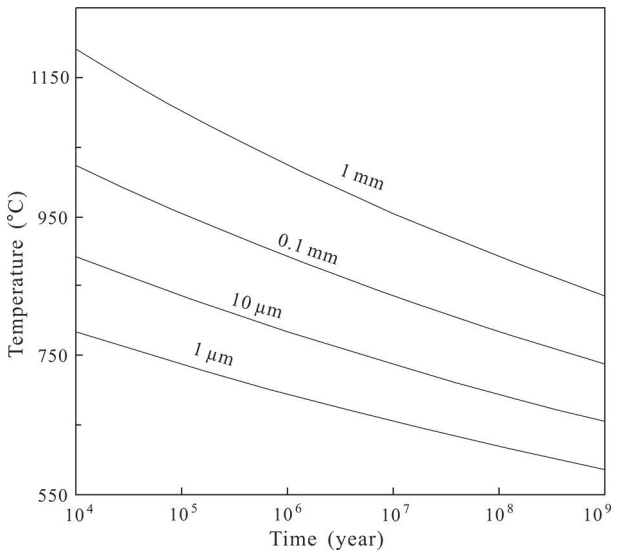


Fig. 5. Preservation of Sm-Nd composition in scheelite grains of various radii.

100 μm over comparable times are 1030°C and 790°C, respectively. At 800°C, Sm-Nd information in the center regions of 1 mm radius scheelite grains will be preserved over time in excess of the age of the Earth. The results of these calculations indicate that scheelite is favourable for retaining its initial Sm-Nd isotope and chemical information under a broad range of conditions if their contents are altered only by diffusion.

Sm-Nd isotopic system of scheelite is commonly used as a geochronometer to constrain the timing of scheelite precipitation or to trace tungsten (-gold) ore genesis. The studied deposits range in age from Archaean to Cenozoic, such as gold-tungsten deposits in the Zimbabwe Archaean Craton (2,668 Ma, 2,604 Ma, and 2,413 Ma; Darbyshire et al., 1996; Oberthür et al., 2000), gold deposits in the Val d'Or area (2,600 Ma; Anglin et al., 1996) and Ontario area (2,400 Ma; Bell et al., 1989) in Canada, the Felbertal tungsten deposit in the central Alps/Austria (581 Ma, 319 Ma and 29 Ma; Eichhorn et al., 1997), the Woxi tungsten-polymetallic deposit (402 Ma; Peng et al., 2003) and Honghuaerji scheelite deposit (178 Ma; Guo et al., 2016) in China, and the Muruntau giant gold deposit in Uzbekistan (351 Ma and 279 Ma; Kempe et al., 2001). According to the dimensionless parameter $Dt/\alpha^2 = 0.03$, scheelite crystal grains of 50 μm effective radius from the Late Archaean and Early Proterozoic gold (-tungsten) deposits mentioned above would hold Sm-Nd signatures during the time span since they were deposited, if their conditioned temperatures were less than 695°C; when at the same temperature over the period of time equal to their mineralization ages, the effective radius limits for scheelite crystals in those Palaeozoic and Mesozoic deposits are of about 25–14 μm; and to the youngest scheelite crystal (29 Ma) in Muruntau giant gold, 50 μm sized grains equilibrate with Sm-Nd in their external surrounding should be heated to temperatures of nearly 780°C. Therefore, except for a very narrow surface layer, the interior regions of macroscopic scaled scheelite crystals (without fractures and surface alteration) from each of those deposits are likely to provide valuable Sm-Nd information unless they have been subjected to extreme heating or have undergone recrystallization.

4.3 REE zones in scheelite

An inhomogeneous distribution in mineral grains that is usually exhibited in the form of compositional zoning (Cherniak, 1995; Paquette and Reeder, 1995; Schönenberger et al., 2008) may record time-temperature histories of hydrothermal systems (Chakraborty and Ganguly, 1992; Ducea et al., 2003; Tirone et al., 2005), and provide insight into the geochemical evolution of ore-forming fluids (e.g., Brugger et al., 2000a; Schönenberger et al., 2008). According to the model of Watson and Liang (1995), the formation of such zoning depends on the diffusion rate (D) of the zoned element within the mineral lattice as well as the growth rate (V) of the crystal. Once the diffusion rate of a zoned element is sufficiently slow relative to the crystal growth rate, development of zoning during growth is unavoidable in crystals that exhibit selective enrichment of the element on specific growth faces.

Compositional zoning in scheelite crystals is frequently observed by cathodoluminescence (CL) spectroscopy, and that often displays highly variable REE contents (Brugger et al., 2000b, 2002; Kozlik et al., 2016; Zhao et al., 2018; Sciuba et al., 2020; Wang et al., 2021). This variation within scheelite zoning can reflect rhythmic changes in the medium from which the mineral crystallizes (Brugger et al., 2000a; Schönenberger et al., 2008; Peng et al., 2010), and has been used to study crystal growth mechanisms (Paterson and Stephens, 1992; Watson and Liang, 1995; Rakovan and Reeder, 1996; Rakovan et al., 1997; Brugger et al., 2008).

Since diffusion can influence the preservation of compositional zoning under a broad range of thermal conditions (Spear and Silverstone, 1983; Ryerson et al., 1989; Watson and Cherniak, 2015), it is paramount to determine the resistance of REEs zoning to the alteration caused by any subsequent thermal events. Assuming zones as planar sheets of thickness l, adjacent planes have different concentrations of diffusant, and concentrations within one zone are initially uniform, simple calculations can be conducted using the above diffusion data to determine which conditions permit Sm-Nd zoning to be changed or preserved. Zones are considered to be "lost" if a compositional change of 10% in the zone's center is determined, and "blurred" when there is an equivalent compositional change 10% of the way into the zone (Cherniak, 1995). The dimensionless parameter Dt/l^2 will be equal to 3.3×10^{-2} when the former condition occurs, and 1.8×10^{-3} when the latter prevails (Crank, 1975).

Fig. 6 shows curves constraining the time-temperature conditions under which Nd (and Sm) zoning of various widths will be maintained in scheelite, given the above criteria. At temperatures of 600°C, for example, 1 μm regions of Sm-Nd zoning would not be "blurred" in about 21 Ma, and "lost" in 393 Ma; whereas time spans for 10-μm zones are 2.1 Ga and greater than the age of the Earth, respectively. At the same temperature, 50-μm Nd zoning

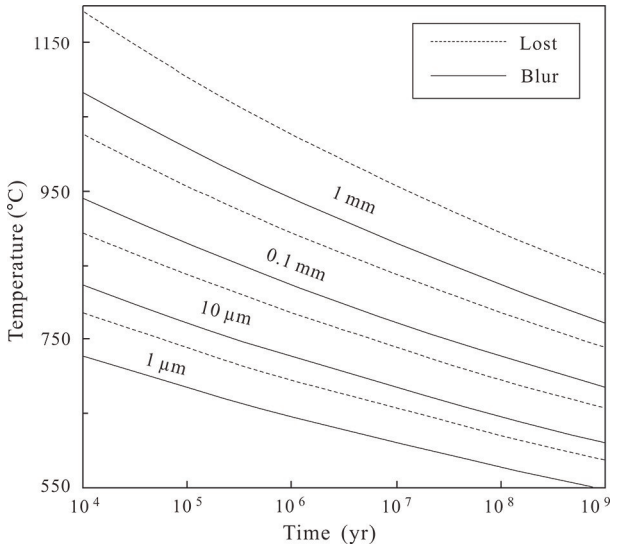


Fig. 6. Preservation of (Sm-) Nd zoning in scheelite.
Curves represent maximum time-temperature conditions under which zoning of different widths will be preserved in scheelite. For conditions above the dashed-line curve in each group, well-defined zoning will be lost; above the solid-line curve, corresponding scale zoning will be blurred but still preserve the initial Sm-Nd information in the zone's center.

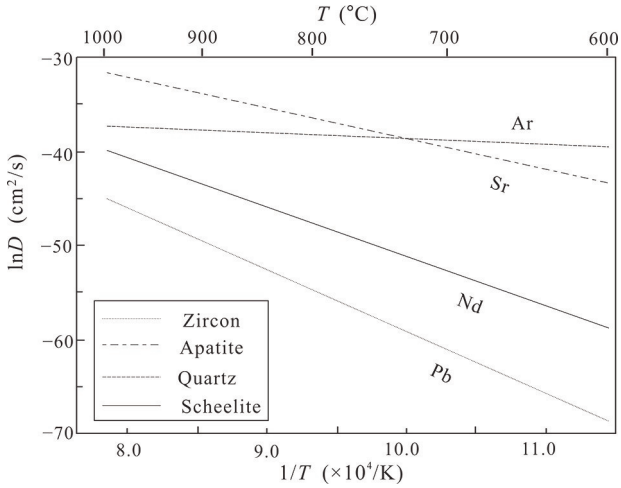


Fig. 7. Comparison of diffusivities for different geochronometers.
Original data include Sr in apatite from Cherniak and Ryerson (1993), Pb in zircon from Cherniak and Watson (2000), Ar in quartz from Watson and Cherniak (2003), and Nd in scheelite as reported here.

would be essentially undisturbed over times in excess of the Earth's evolution history. For Sm-Nd zoning of 100 μm width in scheelite, a temperature of 700°C would ensure it not be "blurred" in 438 Ma and "lost" over a period larger than several Ga, while to persist within scheelite for the same timescales, 150-μm zones would need to be at temperatures of below 715°C, and the corresponding degree value for 200-μm Sm-Nd zoning of about 735°C. Obliteration of Sm-Nd zoning in scheelite would therefore require thermal conditions of relatively high temperatures and/or a long duration. The results of the above calculations are directly applicable to access Sm -Nd zone preservation in scheelite in natural systems. However, it should be noted that this only applies in cases where Nd isotopes and the composition of Sm-Nd systems are affected only by diffusion.

REE zoning have been reported in scheelite from a range of deposits, with zone widths varying from below 1 μm to 200 μm (e.g., Brugger et al., 2000a; Peng et al., 2010; Wang et al., 2021). In many investigations on REE zoning or their inhomogeneous distribution, the beam spots for micro-analyses are generally on the scale of 30–80 μm, such as would be typical of LA-ICP-MS methods (e.g., Brugger et al., 2000a; Schwinn and Markl, 2005; Schönenberger et al., 2008; Zhang et al., 2012a; Ke et al., 2020; Poitrenaud et al., 2020). It is clear that, at this scale, Sm-Nd information in scheelite zoning is modified solely by chemical diffusion.

5 Discussion

Perturbations to a mineral's trace element budget resulting from later alteration processes is determined not only by the degree and length of heating, but also by the diffusion rates of the elemental species in the mineral of interest (Cherniak and Watson, 1994). In order to better interpret the reliability of scheelite Sm-Nd isotopic data obtained in general research studies, in this paper its diffusion behaviors are compared with some excellent geochronometers and isotopic tracers. Fig. 7 is a summary of diffusion data for some mineral-element pairs used commonly in geochemical investigation. The figure illustrates that diffusivities of Sm-Nd in scheelite are intermediate among those geochronometers for which diffusion data exist: i.e., these are faster than for Pb diffusion in zircon, but significantly slower than for either Sr in apatite or Ar in quartz. At a temperature of 600°C, for example, Nd diffusion in scheelite is 4 orders of magnitude faster than for Pb in zircon, but 7 and 8 orders of magnitude slower than Sr in apatite and Ar in quartz. These differences will decrease when diffusion is at a higher temperature, such as when this is at 1000°C, Nd diffuses in scheelite no more than two orders of magnitude faster than for Pb in zircon, and in contrast to the latter two mineral-element pairs, that will decrease to 5 and 4 orders of magnitude more slowly, respectively. This comparison indicates that Sm-Nd systematics in scheelite will not experience a more significant diffusion process than other isotopic methods when exposed to most geological environments. This conclusion is consistent with the previous results that scheelite Sm-Nd data frequently coincide with isotopic ages resulting from other geochronometers (e.g., Eichhorn et al., 1997; Oberthür et al., 2000; Kempe et al., 2001; Peng et al., 2003; Liu et al., 2007; Guo et al., 2016).

Compared to the zircon U-Pb system, Sm-Nd diffusion in scheelite lattice occurs at a faster rate when these are at the same temperatures. While the former is a most excellent isotopic tool by broad consensus, an important factor to consider is that zircon samples used in dating usually were obtained from crystals of less than 100 μm in size, with isotopic data being extracted within zoned regions of ~tens of microns in width, and made by in-situ

methods such as LA-ICP-MS (Horn et al., 2000; Sliwinski et al., 2017) and SHRIMP (Zhou et al., 2002). In contrast, isotopic studies of scheelite are usually made upon samples crushed from macroscopic-sized crystals with effective radii in excess of a millimeter scale. Evidenced by the calculations of closure temperatures and retention times outlined in this study, we suggest that, Sm-Nd in scheelite of effective radius near to 1 mm is comparable to that for zircon of a size typical in dated grains. Accordingly, whether in a slow cooling condition, or subjected to a post-crystallization thermal event, scheelite Sm-Nd systematics is resistant to diffusive composition loss by no more than would be evidenced in zircon.

It is worth pointing out, however, that any influence of water and hydrous species on solid-state diffusion should be also considered. Obvious differences in diffusion constants for Sr in apatite have been observed under anhydrous and hydrous conditions (Farver and Giletti, 1989; Cherniak and Ryerson, 1993), and the presence of water has also been shown to enhance O transport significantly in quartz (Elphick and Graham, 1988), zircon (Watson and Cherniak, 1997), anorthite (Elphick et al., 1988), and upon CaAl-NaSi interdiffusion in plagioclase (Yund and Snow, 1989). Moreover, alteration haloes can facilitate trace element mobility by fluids infiltrating along the rim of mineral grains or within fractures, which would likely cause surface layer(s) of scheelite crystals to differ from their internal portions in terms of REE patterns and Eu anomaly characteristics (Zhang et al., 2012a). Thus, in order to eliminate the effects of water or fluid-based processes, samples for isotopic dating and tracing, no matter for which isotope dilution technique or the in-situ approach used, must be “pristine” and free of alteration. On the other hand, because closure temperatures and retention times will increase with an increase in the effective diffusion radius (Dodson, 1973), it is critical to ensure that the analyzed samples have the best optical quality to gain a high effective radii. Consequently, separated scheelite grains for Sm-Nd isotopic studies should be crushed from larger crystals and examined under the binocular microscope so as to be free of alteration, fractures and/or inclusions.

6 Conclusions

Primary properties for Sm and Nd diffusion in scheelite, as characterized herein, show this mineral to have significant advantages in terms of closure and retention of Sm-Nd systematics within its lattice, that reflect slow rates of diffusion. For this reason, the original Sm-Nd isotopic composition of scheelite is likely to persist under all but the most extreme thermal conditions. When compared with the temperature conditions from many hydrothermal deposits, the results suggest that closure temperatures and retention times for scheelite hold true for Sm and Nd in macroscopic crystals, as these are sufficiently robust. Moreover, our result favour that the related isotopic composition will not have experienced significant changes during either slow cooling or from exposure to the most common geological thermal processes. In this paper, the degree of thermal diffusion influence on Sm-Nd system in scheelite is presented as straightforward numbers, and the obtained results will provide an important theoretical evidence for quantitatively evaluating the reliability of scheelite Sm-Nd dating and tracing data.

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About the first and corresponding author



ZHANG Dongliang, male, born in 1980; lecturer of Central South University. He is now interested in petrogeochemistry and ore deposit geology. E-mail: dlzh04@mails.ucas.ac.cn.