Tracking dynamic hydrothermal processes: Textures, *in-situ* Sr-Nd isotopes and trace element analysis of scheelite from the Yangjiashan vein-type W deposit, South China

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ABSTRACT

Texturally complex minerals can provide critical information on dynamic hydrothermal processes. This study combines cathodoluminescence (CL), laser ablation-inductively coupled plasma mass spectrometry (LA–ICP–MS), and high-resolution femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry (fs–LA–MC–ICP–MS) analyses, to document textures, in-situ Sr-Nd isotope systematics, and trace element compositions of texturally-complex scheelite from the Yangjiashan W deposit, South China. The major motivation for this contribution was to reveal the correlation between CL response, textures, and trace element concentrations; document the origin of various REE fractionation patterns; and to characterize grain scale in-situ variability of Sr-Nd isotopes of scheelite.

Five sub-types of scheelite from both stages, including Sch1 and Sch2 from Stage 1, and Sch3 to Sch5 from Stage 2, are identified. CL images feature complex oscillatory, patchy, and evidence for coupled dissolution-reprecipitation reaction. These scheelites precipitated from reduced fluids and are close to endmember in composition, with Mo concentrations below 46 ppm. Concentrations of other elements vary: Sr (36-1,025 ppm); Nd (8-351 ppm); and Na (7-300 ppm). LA–ICP–MS element maps reveal a large variability in REE concentrations among oscillatory zones, and no consistent behavior between REE, Sr and Mo concentration, and CL intensity. Four distinct chondrite-normalized REE fractionation patterns are recognized: LREE-enriched, MREE-enriched, HREE-enriched, and flat patterns. Complex Eu anomalies (δEu = 0.2 to 20.7) are recognized among the five sub-types and are commonly observed within individual grains. Fluid compositions, different substitution mechanisms (i.e., \( Ca^{2+} + W^{6+} = REE^{3+} + Nb^{5+} \), and \( 2Ca^{2+} = REE^{3+} + Na^+ \), \( 3Ca^{2+} = 2REE^{3+} + \square Ca \), where \( \square Ca \) is a Ca-site vacancy), primary-secondary processes (i.e.,
oscillatory and dissolution-reprecipitation, respectively), all contribute to the variation in REE fractionation patterns. Local fluctuation in fluid pH is responsible for the complex Eu anomalies. In-situ Sr and Nd isotope signatures for the five sub-types of scheelite show relatively large ranges, i.e., the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.71336 to 0.72617, and the initial $\varepsilon$Nd values ranging from -24.9 to -7.7, suggesting a source derived from a mixture of magmatic-hydrothermal fluids and the Neoproterozoic slate. Decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Sch2 to Sch5 record decreasing fluid-rock interaction intensity. Large variation of $\varepsilon$Nd(t) values (-24.9 to -7.7) of scheelite with oscillatory zoning textures may relate to changes of Sm/Nd ratio of scheelite and contamination from wall rock with inhomogeneous Nd isotope composition. This study highlights the importance of performing coupled LA–ICP–MS mapping and in-situ Sr-Nd isotope analyses on sample material that has been characterized in detail at the micron-scale.

**Keywords:** Scheelite, REE fractionation patterns, in-situ Sr-Nd isotope analysis, tungsten deposits, Yangjiashan

**INTRODUCTION**

Appreciating the complexity of hydrothermal processes is critical for accurately constraining the genesis of ore deposits (e.g., Robb 2005). Veins composed of hydrothermal minerals contain integrated information about the hydrothermal fluids, including composition and their migration path through the Earth’s crust. Minerals displaying growth or compositional zoning, such as scheelite, quartz, and sulfides precipitated from hydrothermal fluid, can express the evolution of hydrothermal fluid (Loomis 1983; Shore and Fowler 1996; Brugger et al. 2000; Rusk and Reed 2002; Cook et al. 2009; Barker and Cox 2011). Mineralogical studies bridging nano- to macroscales of observation can thus provide critical information on the ore-forming processes (Cook et al. 2013,
Scheelite, one of the most economically important tungsten minerals, has been widely used to decipher ore-forming processes and sources of fluids and metals (Ghaderi et al. 1999; Brugger et al. 2000, 2002; Poulin et al. 2018; Scanlan et al. 2018; Sciuba et al. 2020). Studies have revealed that scheelite, particularly from magmatic-hydrothermal deposits (e.g., skarns), are commonly heterogeneous with respect to textures (e.g., pronounced oscillatory zoning and dissolution-reprecipitation textures) and trace element distributions at the grain-scale (Song et al. 2014; Poulin et al. 2016, 2018; Sun and Chen 2017; Zhao et al. 2018). Such phenomena carry inference for the interpretation of rare earth element (REE) distribution patterns and isotope systematics (e.g., Sr) which have been proposed as valuable interpretive tools (Brugger et al. 2000, 2002). Despite this, few studies have clearly illustrated the relationships among trace element distributions at the scale of single grains, or between the concentrations of REE (or other trace elements) and the CL response (Poulin et al. 2016; Su et al. 2019).

Scheelite can accommodate measurable amounts of Sm, Nd, and Sr, but negligible Rb (Bell et al. 1989; Kempe et al. 2001). Radiogenic $^{87}$Sr produced from $^{87}$Rb decay is thus insignificant in scheelite, enabling initial $^{87}$Sr/$^{86}$Sr ratios to be preserved (Bell et al. 1989). Considering the grain-scale variability of Sm/Nd ratios due to the heterogeneity in texture and corresponding REE concentrations, together with the progressive fluid-rock interaction which is critical for the formation of tungsten deposits (Wood and Samson 2000; Lecumberri-Sanchez et al. 2017), the Sr and Nd isotope composition of ore-forming fluid will evolve in both time and space, and therefore, any small-scale compositional heterogeneity in scheelite may also be reflected by varying Sr-Nd isotope values (Brugger et al. 2002; Kozlik et al. 2016; Scanlan et al. 2018; Song et al. 2019). For example, different initial $^{87}$Sr/$^{86}$Sr values and $\varepsilon$Nd(t) values were documented among distinct
micro-drilled scheelite separates from a single large crystal with different REE patterns from quartz-vein gold deposits (Brugger et al. 2002). It is, however, unclear thus far to what extent the large variation and overlap in the Sr-Nd isotope data for scheelite displaying heterogeneous textures may be masked by conventional bulk powder chemistry. This observation highlights the necessity of in-situ analyses of coupled Sr-Nd isotope measurements on fully characterized samples in any attempt to better understand the source of metals and dynamic ore-forming processes.

The present study focuses on the Yangjiashan scheelite-quartz vein deposit, a representative tungsten deposit of Paleozoic age in South China (Xie et al. 2019a). We characterize scheelite textures and chemistry, involving specific CL responses and corresponding trace element analyses, including both spot data and element maps determined by laser ablation-inductively coupled plasma mass spectrometry (LA–ICP–MS), coupled with Sr-Nd isotopes analyses determined in-situ by femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry (fs–LA–MC–ICP–MS). We aim to advance understanding of the grain scale in-situ variability of trace element and Sr-Nd isotope distributions in scheelite, thus highlighting the necessity of in-situ analyses of scheelite for correct interpretation of ore-forming processes.

GEological background

The Xiangzhong Sb–Au metallogenic province is located in the southeastern part of the Yangtze Block, South China (Fig. 1a). This province hosts a large concentration of Sb–Au deposits (Hu et al. 2017; Li et al. 2019), including the world-class Xikuangshan Sb deposit, and the Gutaishan and Longshan Au–Sb deposits (Fig. 1b). In addition, two styles of economic tungsten deposits have been discovered and mined, including quartz veins and skarns (Fig. 1b). Quartz vein mineralization is represented by the Yangjiashan scheelite-quartz deposit (Xie et al. 2019a), the Woxi Au–Sb–
scheelite-wolframite-quartz deposit (Zhu and Peng 2015), and the Shaxi scheelite-wolframite-quartz deposit (Su et al. 2016). Tungsten skarns include Caojiaba and Darongxi (Xie et al. 2019b; Zhang et al. 2020).

The Yangjiashan deposit is located at the contact zone between Neoproterozoic rocks and the Baimashan granite (Fig. 2) and has a total $\text{WO}_3$ resource of ~39,000 metric tonnes at an average grade of 0.70% $\text{WO}_3$ (Xie et al. 2019a). Deposit geology has been described by Xie et al. (2019a) and is briefly summarized here. The scheelite-quartz veins are dominantly hosted in psammitic slate of the Mobin Formation, a unit that belongs to the Neoproterozoic Banxi Group (Fig. 2). Intrusions in the Yangjiashan orefield are predominantly by biotite monzogranite (Fig. 2) and represent the northernmost part of the Baimashan pluton (Fig. 1b). SHRIMP U–Pb zircon methods yield an intrusion age of 407 ± 3 Ma, coeval with the Re-Os age of hydrothermal molybdenite (404 ± 3 Ma) intergrown with scheelite (Xie et al. 2019a). Coupled stable isotope compositions, including $\delta^{18} \text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}$ values for quartz (-1.2 to +3.4‰ and -87 to -68‰, respectively), and $\delta^{34} \text{S}$ values of sulfides (-2.9 to -0.7‰), all support a magmatic-hydrothermal fluid source mixed with meteoric water for the Yangjiashan deposit (Xie et al. 2019a).

Two stages of scheelite mineralization are identified (Xie et al. 2019a): early greisen (Stage 1) and late quartz veins (Stage 2) (Fig. 3); the latter represents the major ore type. Greisen ores are composed of quartz, muscovite, scheelite, and arsenopyrite (Fig. 4a, b). The quartz vein-type ores consist of quartz, scheelite, arsenopyrite, chalcopyrite, pyrite, and minor fluorite, cassiterite, and muscovite (Fig. 4c–i). Scheelite grains from both stages occur commonly as cm-sized aggregates with pinkish to whitish color. Mineral assemblages comprising native bismuth and pyrrhotite within quartz veins, and the presence of $\text{CH}_4$ in fluid inclusions hosted within quartz and scheelite (Xie et al. 2019a), suggest scheelite precipitation from relatively reduced fluids in both stages.
A suite of scheelite-bearing samples collected from different mining adit levels, representing both stages of mineralization (Fig. 4), were selected for cathodoluminescence (CL) imaging of grain-scale features, measurement of trace element distributions, and in-situ Sr-Nd isotope analyses. Two samples (YJS-69 and YJS-87; Fig. 4a, b) are from Stage 1, and seven samples (YJS-36, YJS-39, YJS-55, YJS-62, YJS-66, YJS-67, and YJS-71; Fig. 4c–i) are from Stage 2. Detailed characteristics of these samples are described in Supplemental Table S1. Each sample was mounted in epoxy and prepared as a one-inch-diameter polished block.

Scheelite CL images were generated using a FEI Quanta 600 (MLA) with EDX and Gatan CL detectors (Adelaide Microscopy, The University of Adelaide). All measurements were performed at an accelerating voltage of 25 kV and a beam current of ~3 nA.

In-situ LA–ICP–MS trace element spot analysis and mapping of scheelite were obtained using a 213 nm, Q-switched, Nd: YAG New Wave UP 213 laser ablation system, coupled to an Agilent 7900 Quadrupole ICP–MS instrument (Adelaide Microscopy, The University of Adelaide). Data were processed with Iolite using $^{44}$Ca as the internal standard. Operating conditions, isotopes measured, and data processing methodologies are given in Supplemental Table S1, and average minimum detection limits and dwell times are given in Supplemental Table S2.

In-situ Sr and Nd isotope measurements by fs–LA–MC–ICP–MS were performed on a Neptune Plus MC–ICP–MS (Thermo Fisher Scientific, Germany) in combination with a J-200 343 nm femtosecond (fs) laser ablation system (Applied Spectra, USA) housed at the National Research Center for Geoanalysis, Chinese Academy of Geological Sciences (CAGS), Beijing, China. The instrumental mass bias for Sr isotopes was corrected using an exponential law function based on

1 Deposit item
\(^{86}\text{Sr} / {^{88}}\text{Sr}\) value of 0.1194. In-house scheelite reference materials HTPW and XJSW (C. Li et al. 2018) were analyzed every 10 samples. The in-house scheelite reference material (XWC) and Durango apatite (Foster and Vance 2006; Yang et al. 2014) were analyzed for every 10 samples to monitor instrument stability and allow external correction of \(^{147}\text{Sm} / {^{144}}\text{Nd}\) ratios. Detailed data processing methodologies are given in Supplemental\(^1\).

**RESULTS**

*Scheelite textures*

Examination of crosscutting and replacement relationships and textural features allowed recognition of five types of scheelite: Sch1 and Sch2 are from Stage 1; Sch3, Sch4, and Sch5 are from Stage 2. Scheelite from Stage 1 displays a complex CL response in that it exhibits areas of primary growth (Sch1) overprinted by a superimposed type (Sch2) (Fig. 5a). Primary Sch1 is relatively dark in CL response, with clear zonation texture. Sch2 commonly overgrows Sch1 and displays a delicate oscillatory zonation pattern defined by multiple individual zones, each varying from several to tens of micrometers in width (Fig. 5a, b).

Scheelite from Stage 2 has roughly similar but rather complex textures, including oscillatory, patchy, and evidence of dissolution-reprecipitation reaction (Fig. 5c–f). Sch3 is characterized by a well-developed oscillatory zonation pattern, with fluctuation in zone thickness, ranging from several to tens of micrometers in width (Fig. 5c–f). Some Sch3 grains have a bright zoned core and dark zoned rims on CL images, which is overgrown by homogenous Sch4 (Fig. 5c).

Sch4 is commonly homogeneous in CL images (Fig. 5c), although some grains display patchy texture (Fig. 5d, e). Sch4 deposited as rims around Sch3, and the contact boundary between Sch4 and Sch3 is either regular (Fig. 5c) or irregular (Fig. 5e); the latter showing overprinting or
dissolution-reprecipitation textures.

Sch5 shows brighter CL response compared to Sch3 and Sch4, and lacks discernible zonation under CL (Fig. 5c, d). Sch5 either replaces Sch3 (Fig. 5c) or occurs as ‘matrix’ infilling between Sch3 and Sch4 (Fig. 5d).

**Scheelite composition**

Trace element concentration data for the five sub-types of scheelite are summarized in Table 1 and presented in Fig. 6; the full dataset is included in Supplemental Table S3.

Results show that all five sub-types of scheelite are close to endmember in composition, and that Mo concentrations are mostly below 46 ppm (Fig. 6a). Concentrations of Sr, although overlapping, are variable within any individual type (Fig. 6b, c). Measured Sr concentrations range between 85 and 116 ppm for Sch1 (mean 95 ppm), from 49 to 153 ppm for Sch2 (mean 67 ppm), from 42 to 193 ppm for Sch3 (mean 73 ppm), from 36 to 118 ppm for Sch4 (mean 71 ppm), and from 42 to 1,025 ppm for Sch5 (mean 264 ppm) (Table 1). Sodium concentrations show a narrow range for scheelite from Stage 1 (35–186 ppm), in contrast to the scheelite from Stage 2 that displays a relatively large variation (10 to 300 ppm for Sch3, 9 to 250 ppm for Sch4, and <7 to 174 ppm for Sch5, respectively (Fig. 6d, f).

REE concentrations were normalized to chondrite values (McDonough and Sun 1995) and are shown in Figure 7. Analyzed scheelites can be grouped into four distinct types according to their REE patterns: LREE-enriched, MREE-enriched, HREE-enriched, and flat patterns (Fig. 7). Sch1 from Stage 1 (Fig. 5a) features a LREE-enriched pattern with \((La/Yb)_N\) values ranging from 4.6 to 9.6 (Fig. 7a), accompanied by weak positive Eu anomalies (\(\delta Eu = 1.0 \text{ to } 2.2\)). Total REE concentrations range between 938 and 1,172 ppm (mean 1,015 ppm), and the measured Nd...
contents vary between 203 and 248 ppm (mean 220 ppm) (Table 1).

Sch2 from Stage 1 is characterized by HREE-enriched pattern with (La/Yb)$_N$ values below 0.4, and both positive and negative Eu anomalies, with Nd concentrations between 41 and 157 ppm (mean 86 ppm) (Table 1). Sch2 overgrowth on Sch1 (Fig. 5a) mostly feature weak positive Eu anomalies ($\delta$Eu = 0.8 to 1.6) (Fig. 7a, Sample YJS-69), with total REE concentrations between 522 and 1,082 ppm (mean 892 ppm) and (La/Yb)$_N$ values ranging from 0.17 to 0.36. In contrast, Sch2 occurring as isolated grains (Fig. 5b) has negative Eu anomalies ($\delta$Eu = 0.2 to 0.9) (Fig. 7a, Sample YJS-87) with total REE concentrations between 524 and 818 ppm (mean 659 ppm), and relatively lower (La/Yb)$_N$ values (0.02 to 0.16).

Scheelite from Stage 2 is characterized by site-specific REE fractionation patterns (Fig. 7b–i), with no single distinctive REE pattern recognizable, particularly for the zoned Sch3 sub-type. Sch3 features a broad variety of REE patterns (Fig. 7b–f) and both negative and positive Eu anomalies ($\delta$Eu = 0.2 to 14.7), with (La/Yb)$_N$ values ranging from <0.1 to 10.1. Total REE concentrations range between 184 and 1,801 ppm (mean 911 ppm), and Nd concentrations from 21 to 351 ppm, with a mean value of 154 ppm (Table 1). The distinct micron-scale zones within individual grains (e.g., Sample YJS-55, Fig. 5d) show markedly different REE patterns and variable Eu anomalies (Fig. 7c).

Similar to Sch3, Sch4 and Sch5 also display complex REE patterns with (La/Yb)$_N$ values ranging from 0.1 to 8.2, and both positive and negative Eu anomalies ($\delta$Eu = 0.3 to 20.7 and 0.2 to 2.5 for Sch4 and Sch5, respectively) (Fig. 7g–i). Total REE concentrations range from 98 to 1,609 ppm for Sch4 (mean 788 ppm), and from 51 to 1,243 ppm for Sch5 (mean 407 ppm). The measured Nd concentrations vary from 10 to 323 ppm for Sch4 (mean 129 ppm), and from 8 to 278 ppm for Sch5 (mean 85 ppm) (Table 1).
Trace element mapping

LA–ICP–MS trace-element maps (Figs. 8 and 9) are used to further visualize the chemical heterogeneity behind the observed CL-defined zonation in two representative scheelite grains with complex REE fractionation patterns from Stage 2 (Samples YJS-55 and YJS-67). Scheelite from Stage 1, which has relatively consistent REE fractionation patterns (Fig. 7a), was not mapped.

The mapped area from sample YJS-55 contains Sch3, Sch4, and Sch5, and they display contrasting CL intensity (Fig. 8). Sch3 shows distinct chemical heterogeneity for most mapped elements, and is relatively enriched in MREE, HREE, Nb, and Na compared to Sch4 and Sch5. MREE appear to show an oscillatory distribution pattern and show a decoupling between Eu and other elements. Maps for Na, Mn, and Pb show that these elements are enriched as patches rather than across the entire grain. Niobium shows an oscillatory distribution pattern in Sch3, whereas the distribution of Mo is irregular. Compared to Sch3 and Sch5, Sch4 is relatively enriched in La, Ce, Eu, and U. Except for Eu and Lu, other MREE and HREE are at low concentrations. Sch5 is relatively depleted in all trace elements except Sr. Interestingly, the distribution of Sr does not follow the same chemical zones as delineated by other elements (e.g., REE, Mo, and Mn).

Sample YJS-67 contains Sch3 with a pronounced oscillatory zoning (Fig. 9). The upper part of the mapped area appears brighter than the lower part in CL image. This difference in brightness may, however, be an artefact arising from the electron-beam detector geometry. Although the two parts of the grain appear discontinuous in the CL image, element maps show a continuous distribution of most elements, including MREE, HREE, Mo, Nb and U, across the boundary between the two domains. The maps reveal a large variability in REE concentrations between zones, and, moreover, a discontinuous distribution of LREE (La, Ce, and Pr) within zones. We also note that Eu is relatively enriched in the inner zones, in contrast to the distribution patterns shown by Mo.
and Pb. Mapping also reveals that Na, Mn, and Sr are irregularly distributed.

In-situ Sr-Nd isotope composition of scheelite

Sr-Nd isotope data for scheelites from the Yangjiashan deposit are summarized in Tables 2 and 3, respectively, and shown as Figure 10. The full dataset is included as Supplemental1 Tables S4 and S5. All Nd isotope compositions were also recalculated to 400 Ma (Xie et al. 2019a) due to decay of $^{147}\text{Sm}$ to generate $^{143}\text{Nd}$. Measured values for Durango apatite and other reference materials match standard values well. Together with the good reproducibility, any possibility of analytical artefacts can be precluded. Depending on Sr content, the signal intensity for $^{88}\text{Sr}$ ranges from 0.31 to 5.81 V (Fig. 10a), The uncertainty of all $^{87}\text{Sr}/^{86}\text{Sr}$ values varied from 0.00007 to 0.0009 (2σ), displaying an inverse correlation with Sr content, which is manifested by the signal intensity of $^{88}\text{Sr}$ (Fig. 10a).

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Sch1 to Sch5 range from 0.71336 to 0.72617 (Fig. 10b). The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for Sch1 to Sch5 are from 0.09147 to 0.29343, and from 0.51085 to 0.51173, respectively (Fig. 10c). Calculated initial εNd(t) values range from -24.9 to -7.7 (Fig. 10d).

**DISCUSSION**

Correlation between textures observable by CL imaging and trace element distributions

Combining trace element maps with textures imaged by CL gives invaluable insights into the nature of ore-forming fluids and allows reconstruction of the growth history of minerals like scheelite. Scales of observation and spatial resolutions are similar, allowing direct comparison between element concentrations and CL intensity over relatively large areas of individual grains.

The role played by Mo in modifying the intensity of the CL response of scheelite remains uncertain. In samples studied here, Mo-depleted Sch5 domains have a brighter CL response than...
Mo-enriched Sch3 and Sch4 (Fig. 8), consistent with the observation that a decrease in the CL intensity occurs with increased Mo content due to a greater distortion of the crystal structure (Poulin et al. 2016). We speculate, however, that while this correlation is essentially correct, it may not be exclusively so because some fluctuations of CL intensity occur independently of Mo concentration variation when Mo concentrations in scheelite reach >10,000 ppm, such as in the Zinnwald–Cínovec Sn–W–Li greisen-type deposit, Germany-Czech Republic (Poulin et al. 2016). LA–ICP–MS element maps of scheelite from the Dabaoshan porphyry Mo–W deposit, South China (Su et al. 2019), also reveal more complex relationships between CL intensity and Mo content. We therefore conclude that substitution of Mo for W, at the grain-scale, has an inconsistent effect on the CL response of scheelite. Although incorporation of Mo will decrease the self-activated emission band effectiveness that is correlated to W content, other factors such as incorporation of REE and Pb which cause lattice distortion, all have influence on CL response (Macrae and Wilson 2009; Poulin et al. 2016).

Whether Sr plays a role in modifying the intensity of the CL response of scheelite remains unclear thus far, even though data compilations have shown that scheelite from different geological settings can be distinguished by markedly different Sr content and REE characteristics (Poulin et al. 2018; Sciuba et al. 2020). For example, a maximum of 11,480 ppm, and mean value of ~2,232 ppm Sr has been given for orogenic gold deposits compared to an overall average of 387 ppm for magmatic-hydrothermal deposits (Poulin et al. 2018). The maps of Sch3 with oscillatory variation in CL intensity among growth zones (Figs. 8 and 9) show no concordant measurable variation in Sr concentration. Both positive or negative correlation between Sr concentration and CL intensity have been observed elsewhere (Poulin et al. 2016; Su et al. 2019). Collectively, these observations suggest no direct cause and effect relationship between Sr concentration and CL intensity within
individual scheelite grains, although incorporation of Sr might cause intrinsic defects in scheelite due to its electronic configuration (Poulin et al. 2016).

Incorporation of REE has also been demonstrated to exert an influence on CL intensity, and scheelite from different mineralization settings can be distinguished by their CL textures and REE fractionation patterns. For example, scheelite from orogenic gold deposits commonly shows homogenous CL images and has a MREE-enriched but otherwise flat pattern (Poulin et al. 2016; Sciuba et al. 2020). Likewise, LREE-enriched patterns appear to be a feature of magmatic-hydrothermal deposits such as skarns and porphyry systems. Scheelite from these deposits are characterized by complex (e.g., oscillatory) CL responses (Song et al. 2014, 2019; Poulin et al. 2016; Sun and Chen 2017; Zhao et al. 2018). Figures 8 and 9 show no general relationship between scheelite CL intensity and REE concentrations, highlighting the interplay between individual REE$^{3+}$, such as Eu and Tb. In other words, the resulting CL response depends on the intensity ratios of these activators and is thus not an unambiguous characteristic of one element or the other (Nazarov et al. 2004; Macrae et al. 2009; Götze 2012). Our study nevertheless provides ‘snapshot’ information about the importance of element maps in revealing the heterogeneous distribution of REE in scheelite displaying complex CL intensity variation. Because our analyses reflect bulk CL intensities (the combined result of CL intensities at different spectral emissions), and due to a lack of qualitative CL spectra data, an unequivocal determination of which REE plays the most important role in controlling the CL response observed is hindered.

In summary, except for the overwhelming nature of the self-luminescence band attributed to WO$_4^{2-}$ tetrahedra, trace elements incorporated into scheelite, including Mo, Sr, or REE, have, by themselves only inconsistent effects on the CL response. Both intrinsic (e.g., the self-activated emission band and structural defects) and extrinsic defects (e.g., trace element incorporation) are

**Origin of distinct REE fractionation patterns**

The various measured REE fractionation patterns in scheelite from the Yangjiashan deposit suggests that although there are clearly generalized trends with global significance as summarized above, heterogeneity within a single deposit, or even among grains in the same sample, may show variation that overlaps with these general trends (Fig. 7). We suggest that coexisting Ca-bearing minerals and temperature both have insignificant effects on REE fractionation.

Previous studies have shown that the presence of coexisting Ca-bearing minerals such as garnet and diopside can impact on the REE fractionation patterns of scheelite, particularly in skarns (e.g., Song et al. 2014; Zhao et al. 2018). We examined the mineral assemblages associated with scheelite and note that the most abundant minerals associated with scheelite are quartz and sulfides (arsenopyrite and pyrite) (Fig. 4), accompanied by very small amounts of fluorite (Fig. 4c). Consequently, we anticipate no significant change in the concentrations of REE in fluid and negligible impact on the preferred partitioning of LREE or HREE to be induced by the presence of Ca-bearing minerals. Temperature is an important control on the mobility of the REE in fluid (Migdisov et al. 2016). We discount the temperature factor because measured homogenization temperatures are mostly within a narrow range (200 to 270 °C; Xie et al. 2019a).

We propose that: (1) fluid compositions; (2) different substitution mechanisms; and (3) hydrothermal replacement processes (e.g., dissolution-reprecipitation) are all responsible for the range of REE fractionation patterns observed in Yangjiashan scheelite. The development of wall-rock alteration accompanying vein formation, combined with the extreme variations in Sr and Nd isotope compositions in the Yangjiashan deposit (Fig. 10), provide evidence for an open
mineralizing system. Published case studies have shown that, in a closed system, scheelite shows
gradual changes from MREE-enriched to MREE-depleted patterns (Brugger et al. 2000). Changes
in REE fractionation patterns in this study cannot be explained by the closed system crystallization
advocated by Brugger et al. (2000).

1 Fluid composition. Sch1 and the Baimashan pluton have similar REE patterns (Fig. 7a),
suggesting that scheelite inherits its REE composition from the ore-forming fluid, a plausible
explanation that has been applied in the interpretation of some W skarns (e.g., Song et al. 2014; Sun
and Chen 2017). In addition, scheelite preferentially incorporates LREE over HREE due to ionic
radii considerations (Poulin et al. 2018), a potential mechanism that contributes to the observed
LREE-enrichment in Sch1. Calculated LREE/HREE values for granite and Sch1 range from 4.2 to
16.9 (with a mean value of 12.3; Yang et al. 2015), and from 5.9 to 10.1 (with a mean value of 8.1;
Supplemental1 Table S3), respectively. Sch1 crystallization, assuming low fluid-rock interaction
during Stage 1, would shift the residual fluid to relative LREE enrichment, thus allowing deposition
of HREE-depleted Sch2. However, this is in contrast with HREE-enriched Sch2 (Fig. 7a),
indicating that the original magmatic REE signature has been modified during fluid-rock interaction,
a process that is supported by the Sr and Nd isotope signatures (Fig. 10b, d).

2 Different charge balance mechanisms. The substitution $\text{REE}^{3+} \leftrightarrow \text{Ca}^{2+}$ is not isovalent,
hence, a mechanism of charge balance is required. Three main mechanisms for REE substitution of
Ca have been proposed (Nassau and Loiacono 1963; Ghaderi et al. 1999; Brugger et al. 2000):

\[ \text{Ca}^{2+} + \text{W}^{6+} = \text{REE}^{3+} + \text{Nb}^{5+} \quad (1); \]
\[ 2\text{Ca}^{2+} = \text{REE}^{3+} + \text{Na}^+ \quad (2); \]
\[ 3\text{Ca}^{2+} = 2\text{REE}^{3+} + \square \text{Ca}, \text{ where } \square \text{Ca is a Ca-site vacancy} \quad (3). \]

For mechanism (1), binary plots of the mole fraction of REE against Nb display a generally
positive correlation, and some spots of Sch2, Sch3 and Sch5 are close to the 1:1 correlation line (Fig. 6e). This indicates that the coupled substitution in equation (1) are applicable to some scheelites (Zhao et al. 2018). This hypothesis is further supported by relatively high concentrations of Nb, exceeding 240 ppm (Fig. 6e). Given the fact that the radius of Nb$^{5+}$ (0.48 Å) is closer to that of Mo$^{5+}$ (0.46 Å) than Mo$^{6+}$ (0.41 Å) (Shannon 1976), incorporation of Nb could have been coupled to the concentration of Mo$^{5+}$ in scheelite under relatively reduced conditions (Zhao et al. 2018). We also note that Nb incorporation may favor substitution of HREE or MREE over LREE based on spot and mapping results (Figs. 8 and 9), leading to a series of diverse REE patterns (Fig. 6e).

For mechanism (2), Ghaderi et al. (1999) and Brugger et al. (2000) suggested that if Na in the fluid is sufficiently high (>60 ppm) to provide the charge balance in scheelite, considering that Na can incorporated into scheelite based on Goldschmidt’s rules (Na$^{+} = 1.18$Å, Ca$^{2+} = 1.12$ Å; Shannon 1976), MREE would preferentially substitute into the Ca site. In this study, some Sch1 and Sch5 plot close to the ideal 1:1 correlation line (Fig. 6f), supporting the coupled substitution in equation (2). Most data plot away from the 1:1 correlation line, however (Fig. 6f), indicating that equation (2) cannot be the dominant substitution mechanism.

For mechanism (3), we prefer to explain the flat REE patterns (Fig. 7e) in terms of REE incorporation in scheelite via a Ca-site vacancy mechanism, enabling REE$^{3+}$ incorporation into these scheelites independently of ionic radius (Nassau and Loiacono 1963; Ghaderi et al. 1999). Changes from MREE-enriched patterns to flat patterns via the fractional crystallization model proposed by Brugger et al. (2000) might be unsuitable for the Yangjiashan deposit, because significant changes in pattern are observed from scheelite with oscillatory texture (Fig. 11). Shifting a local maximum from MREE to HREE is more likely to be related to site distortion in the Ca$^{2+}$ site caused by the replacement of Ca$^{2+}$ by Sr$^{2+}$ or other elements with relatively large ionic radii such as...
the detectable Pb\(^{2+}\) (Ghaderi et al. 1999; Poulin et al. 2018).

(3) **Primary-secondary processes.** Scheelite with primary textures such as oscillatory zoning and secondary textures such as evidence for dissolution-reprecipitation reaction (Figs. 5 and 11), provide an opportunity to illustrate REE behavior during these processes. It has been suggested that oscillatory zoning is either caused by extrinsic changes in the parent hydrothermal system, such as varying fluid composition, pressure or temperature, or is associated with intrinsic mechanisms linked to diffusion and growth rate (Loomis 1983; Shore and Fowler 1996). Scheelite with oscillatory texture showing either insignificant or significant variations in REE patterns among different grains (Fig. 11a–d), may suggest that the REE signatures alone cannot be used to make inferences about extrinsic chemical changes in the fluid from which scheelite precipitated. If REE enters these scheelite grains via coupled extrinsic and intrinsic mechanisms, the validation of which warrants further investigation, it becomes more difficult to clearly link information recorded by the REE to ore-forming processes. The data for scheelite from the Yangjiashan deposit represents an example of how the REE patterns of Ca-minerals with complex grain-scale textures (e.g., apatite) can be linked to hydrothermal processes and identify the fluid source. The complex patterns do, however, challenge the role of REE fractionation patterns as a discriminator of ore deposit genesis.

Moreover, the observed dissolution-reprecipitation textures hint at REE mobility during secondary processes. Sch5 occurring within Sch3 that may have formed via dissolution-reprecipitation processes shares similar REE fractionation patterns to those of the precursor Sch3 (Fig. 11e, f). In contrast to these, Sch5 precipitated as overprinting rims has a distinct REE fractionation patterns compared to earlier types (Fig. 11g, h). Such a contrast in REE fractionation patterns for these two types of Sch5 reflect the multiple controlling factors on REE properties as discussed above.
Source and nature of ore-forming metals and fluids

Age-corrected (400 Ma) initial whole rock \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratios and \( \varepsilon\text{Nd}(t) \) isotope composition of the Banxi Group slate display wide ranges (0.71085 to 0.73462 and -16.6 to +0.3, respectively), overlapping that of the Baimashan intrusion (0.71671 to 0.71682 and -12.2 to -12.0, respectively; Supplemental\(^1\) Tables S6 and S7) (Fig. 10b, d). The Baimashan granite has been interpreted to be derived from partial melting of Neoproterozoic crustal rock (Shu et al. 2006; Chu et al. 2012).

Several lines of evidence support a close genetic relationship between mineralization and the host granite. These include: (1) overlapping ages – intrusion and mineralization both took place at ~404 Ma (Xie et al. 2019a); (2) isotope compositions, such as the H and O isotope signatures of quartz, indicating that ore-forming fluids originated mainly from granite, with input of meteoric water (Xie et al. 2019a); and (3) similar REE pattern of Sch1 and the Yangjiashan granite (Fig. 7a). We deduce that the most probable source of Sr and Nd for all scheelite sub-types is a mixing of magmatic-hydrothermal fluids following interaction with host rock (Fig. 10b, d).

The accurate determinations of in-situ Sr-Nd isotope compositions by fs–LA–MC–ICP–MS (C. Li et al. 2018), make it an ideal method for tracing the fluid evolution path and for estimation of the source of ore-forming metals (Foster and Vance 2006; Yang et al. 2011, 2014; Kozilık et al. 2016). In the Yangjiashan deposit, the different populations of \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratios in scheelite show a broadly decreasing trend from Sch2 to Sch5 (Fig. 10b). The broadly decreasing Sr isotope compositions may be explained as follows. (1) Scheelite from greisen ores (Stage 1) was precipitated under a more intensive wall rock alteration regime than scheelite from quartz veins (Stage 2). The structural control of quartz veins indicates channelized fluid migration along faults or cracks (Sibson 1994; Robb 2005). A greater proportion of Sr from wallrock is recorded in Stage 1 than Stage 2. (2) The Neoproterozoic Banxi Group slate displays a very large range of Sr isotope compositions (Fig. 10b).
therefore, incongruent leaching of radiogenic Sr in altered host rock may have contributed to this
conclusions have been reached to interpret the regional Sr isotope variations in scheelite from
orogenic Au–W deposits hosted in greenschist/grayschist with different Sr isotope composition,
Otago Schist, New Zealand (Scanlan et al. 2018).

The εNd(t) data for Sch1 and a sub-population of Sch2 are depleted relative to the Baimashan
granite, indicating mixing with Banxi Group slate with low εNd(t) values during Stage 1 (Fig. 10d).
The εNd(t) values for Sch3 range widely, and together with the oscillatory textures in these
scheelite types, point to a primary origin for the isotopic variations, i.e., they reflect isotopic
variations in the hydrothermal fluids from which the scheelite precipitated (Brugger et al. 2002).
The large variation of εNd(t) values, particularly for these low εNd(t) values, are distinct from the
age-corrected (400 Ma) εNd(t) values of the Banxi Group slate (Fig. 10d). Fluorite (Fig. 4c) and
REE-bearing minerals occur as inclusions within scheelite (Supplemental1 Fig. A1). Both are
candidates that could induce similar effects as bastnäsite (Brugger et al. 2002), in that their
deposition would disturb the Sm/Nd ratio of ore-forming fluid, causing an erroneous extrapolation
from measured $^{143}$Nd/$^{144}$Nd to a spurious initial $^{143}$Nd/$^{144}$Nd at 400 Ma. Similar cases have been
observed in scheelite from gold deposits, for example, anomalous εNd(t) signatures described by
Ghaderi (1998) and Brugger et al. (2002). The two endmember modeling results indicate that the
measured Sr and Nd isotope compositions of scheelite show deviation from the mixing line (Fig.
12), providing an additional indication that disturbance of the Sm/Nd ratio in fluid contributed to
the large variation observed.

At Stage 1, although the REE pattern of the Yangjiashan granite and Sch1 are similar, their δEu
values are distinct: negative for granite (0.52–0.71; Yang et al. 2015); and neutral or positive for
Sch1 (1.0~2.2; Fig. 6a). This difference in the sign of Eu anomalies may reflect hydrothermal fluids with some modifications by reaction with wall rock and input of meteoric water (Brugger et al. 2002; Sun and Chen 2017). This is supported by the fact that the greisen mineralization is the product of fluid interaction with wall rock (Fig. 4a, b) and the H and O isotope signatures (Xie et al. 2019a).

During Stage 2, we propose that local pH fluctuation is responsible for the complex Eu anomalies observed. Case studies have shown that the oxidation state of trace elements (e.g., Eu) incorporated in hydrothermal minerals provides an additional tool to constrain the nature of fluids, such as pH (Brugger et al. 2008). According to modelling (Brugger et al. 2008), results show that under the same $f_{O_2}$ and temperature, a drop/increase in fluid pH of ~0.3 unit will lead to the Eu$^{2+}$/Eu$^{3+}$ ratios in scheelite shifting from 1.0 to 7.3, hence, the oxidation state of Eu in scheelite could be a sensitive tracer of fluid pH. During fluid-rock interaction, mixing with meteoric water, together with fluid boiling processes resulting in loss of CO$_2$ (Supplemental Fig. A2), fluid pH will change (Wood and Samson 2000), causing large variations in the size of Eu anomalies in scheelite (Fig. 13). Progressive fluid-rock interaction is also manifested by the in-situ Sr and Nd isotope signatures discussed above. The lower total REE concentrations of Sch5 (Fig. 11g, h) may also record mixing with meteoric water, a component that normally has very low REE contents. Input of meteoric water is further evidenced by the H-O isotope compositions of quartz coexisting with scheelite (Xie et al. 2019a). Changes in fluid redox state related to the variations in the Eu$^{2+}$/Eu$^{3+}$ ratios preserved in scheelite is negligible, considering scheelite in the Yangjiashan deposit precipitated from relatively reduced fluids with narrow ranges in $f_{O_2}$ (Supplemental Fig. A3).
Implications for the study of scheelite

Firstly, coupled in-situ Sr-Nd isotope analyses are of great advantage in illustrating the source of ore-forming metals and tracing dynamic hydrothermal processes. In this study, the Sr-Nd isotope compositions for all types of scheelite display relatively large variations, particularly for Sch3, which displays oscillatory texture and complex REE fractionation patterns (Fig. 11). These variations implicitly suggest that conventional bulk powder analysis of Sr and Nd isotope compositions may be problematic for texturally complicated scheelite.

Secondly, Sm-Nd dating of scheelite should be carried out with caution. Absolute age determinations using the Sm-Nd isotope system assume that the fluid is homogeneous with respect to initial $^{143}\text{Nd}/^{144}\text{Nd}$, and that minerals have remained closed systems with respect to Sm and Nd since crystallization (Dickin 2005). This study suggests that a fluid system with heterogeneous $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ composition for texturally complex scheelite also challenges the meaning of Sm-Nd scheelite ages (Fig. 10c). For example, in the Mount Charlotte Au ± W deposit, the Sm-Nd scheelite age of 2,772 ± 86 Ma determined by conventional bulk powder methods (Kent et al. 1995), is older than the age of hydrothermal muscovite (2,602 ± 8 Ma; Kent and McDougall 1995). These different ages and the corresponding time gaps between metamorphism, magmatism and Au mineralization contribute to the observed diversity of ages and equivocality on ore genesis.

We suggest that micron- to nano-scale textural investigation, together with a preliminary round of (fs)-LA–ICP–MS trace element analysis to determine variations in Sm and Nd concentrations and isotope ratios, should be undertaken prior to conducting conventional or in-situ Sm-Nd isotope analysis. Grains or points should be selected for isotopic analysis to cover the full range of Sm/Nd ratios present.
CONCLUSIONS

1. Fluid compositions, different substitution mechanisms, primary, and secondary processes, all contribute to the variation in observed REE fractionation patterns. Concentrations of Mo, Sr, or REE in scheelite cannot individually be linked to differences in CL intensity. Local pH fluctuation is suggested to be responsible for complex Eu anomalies.

2. Large variations in Sr and Nd isotope compositions of scheelite suggest that the Yangjiashan deposit derived from a mixing of magmatic-hydrothermal fluids following interaction with the Neoproterozoic slate. Fluid-rock interaction, changes in fluid composition, and a disturbance of Sm/Nd ratios in fluid induced by precipitation of fluorite and REE-bearing minerals. Each of these factors contribute to the observed large variations in Sr and Nd isotope compositions. Sm-Nd dating of scheelite should be carried out with caution and an in-depth understanding of the grains selected for analysis.

3. Texturally-complex scheelite provides critical information on the dynamics of hydrothermal systems, highlighting the value of combining LA–ICP–MS mapping and in-situ Sr-Nd isotopes analysis on well characterized samples to illustrate the source of ore-forming metals and trace evolving hydrothermal processes.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

FIGURE 1. Geological map of the Xiangzhong Sb–Au metallogenic province, showing the most important ore deposits and intrusions. Map modified after W. Li et al. (2018).

FIGURE 2. (a) Geological map of the Yangjiashan deposit, and (b) representative cross section along exploration line (A–B) showing the occurrence and morphology of the major orebodies of the Yangjiashan deposit (modified after Xie et al. 2019a).

FIGURE 3. Photographs showing the different stages of tungsten mineralization from the Yangjiashan deposit. (a, b) Greisen ores within granite and Banxi Group slate, respectively. (c, d) Scheelite-bearing quartz veins within the granite and Banxi Group slate, respectively. Qz–quartz; Sch–scheelite.

FIGURE 4. Photographs showing the occurrence of two types of ores. a and b are from the greisen ores; c and d are from the quartz vein-type ores. (a, b) Arsenopyrite, quartz, muscovite coexists with scheelite. (c) Sulfides assemblage containing arsenopyrite and pyrite coexists with scheelite, and minor fluorite within the quartz vein. (d) Scheelite and coexisting muscovite located at the contact between quartz vein and adjacent silicified slate. (e) Scheelite-bearing quartz vein within silicified granite. (f) Scheelite coexisting with cassiterite within the quartz vein. (g) Coarse-grained scheelite assemblage within the quartz vein. (h) Thin veins containing chalcopyrite, pyrite and scheelite within strongly silicified slate. (i) Scheelite and coexisting arsenopyrite and pyrite within the quartz vein. Apy–arsenopyrite, Cp–chalcopyrite, Cst–cassiterite, Fl–fluorite, Ms–muscovite, Py–pyrite, Qz–quartz, Sch–scheelite.

FIGURE 5. Cathodoluminescence (CL) images showing textures features of scheelite from both stages. a and b are from greisen ores; c–f are from quartz vein-type ores. (a) Subhedral Sch2 with oscillatory texture overgrowing Sch1. Sch1 displaying weak zonation. (b) Euhedral Sch2 with oscillatory texture. (c) Textural features of different types of scheelite from Stage 2. Sch3 showing oscillatory texture characterized by bright and dark zones. Sch4 with homogeneous texture overgrowing Sch3. Sch5
replacing the earlier two types of scheelite. (d) Euhedral Sch3 with well-developed oscillatory texture
overprinted by patchy Sch4, then both Sch3 and Sch4 overprinted and replaced by Sch5. (e) Sch3
irregularly overprinted and replaced by Sch4. (f) Sch3 with weak oscillatory zoning. Sch–scheelite.

**Figure 6.** Plots showing variation in the concentration of selected trace elements from the different types of
scheelite. See text for additional explanation.

**Figure 7.** Chondrite-normalized REE fractionation patterns of scheelite from the Yangjiashan deposit. REE
data of Baimashan granite from Yang et al. (2015) are shown for comparison.

**Figure 8.** LA–ICP–MS element maps of representative scheelite including Sch3, Sch4, and Sch5 from Stage
2 quartz vein, showing the distribution of REE and other trace elements. Scales in counts-per-second
(cps).

**Figure 9.** LA–ICP–MS element maps of representative Sch3 with oscillatory texture from Stage 2 quartz
vein, showing the distribution of REE and other trace elements. Scales in counts-per-second (cps).

**Figure 10.** Plots showing variation in Sr and Nd isotopes from different types of scheelite. See text for
additional explanation.

**Figure 11.** Representative CL images showing the texture of scheelite and corresponding variations in
chondrite-normalized REE fractionation patterns. All grains are from Stage 2.

**Figure 12.** Plot of εNd(t) vs. $^{87}\text{Sr}/^{86}\text{Sr}$ showing the features of scheelite. The endmember mixing curve was
made assuming the Banxi Group with the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and lowest εNd values, or the Banxi Group
with the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and εNd values, respectively. The box means the ranges for Sr and Nd isotope
compositions.

**Figure 13.** Plot of chondrite-normalized Eu concentrations ($\text{Eu}_N$) against calculated $\text{Eu}_N^*$ values of scheelite
from the Yangjiashan deposit. Note that $\text{Eu}_N^* = (\text{Sm}_N \times \text{Gd}_N)^{1/2}$. Dashed line represents δEu ($\delta\text{Eu} = \text{Eu}_N/\text{Eu}_N^*)$ values.

**Supplementary Material**

**Supplementary**

**Table S1.** Description of samples discussed in the present study

**Table S2.** Average minimum detection limits and dwell times for LA–ICP–MS spot analysis and mapping

**Table S3.** Laser ablation inductively coupled plasma mass spectrometry trace element data for scheelite
from the Yangjiashan deposit (ppm)

TABLE S4. Complete in-situ Sr isotope dataset for scheelite from the Yangjiashan deposit

TABLE S5. Complete in-situ Nd isotope dataset for scheelite from the Yangjiashan deposit

TABLE S6. Complete dataset of whole rock Sr isotope data for wallrock and granite

TABLE S7. Complete dataset of whole rock Nd isotope data for wallrock and granite

FIGURE A1. REE-bearing minerals within scheelite

FIGURE A2. Vapor-rich and liquid-rich fluid inclusions co-existed within scheelite and quartz from Stage 2

FIGURE A3. Log $\alpha$H$_2$S versus log $f$O$_2$ diagrams showing the fields of stability for sulfides
Table 1. LA–ICP–MS data for scheelite from the Yangjiashan deposit (ppm)

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Note: bdl signifies that measured data are below minimum detection limits.
TABLE 2. Measured *in-situ* Sr isotope data for scheelite from the Yangjiashan deposit

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Note: (v) means voltages for Rb and Sr isotope measurement
### Table 3. Measured *in-situ* Nd isotope data for scheelite from the Yangjiashan deposit

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Note: $^{143}$Nd/144Nd (400) = $^{143}$Nd/144Nd (0) - $^{147}$Sm/144Nd × (Exp ($\lambda_{Sm} \times 400$ Ma ×1000000) - 1), εNd (400) = (($^{143}$Nd/144Nd (400)$_{sample}$/$^{143}$Nd/144Nd$_{CHUR}$) - 1)*10000. The values for $\lambda_{Sm}$ and $^{143}$Nd/144Nd$_{CHUR}$ are $6.54 \times 10^{-12}$ and 0.512638, respectively.
Figure 3
Figure 11
Figure 13