

Inhomogeneous distribution of *REE* and initial Nd isotopic compositions in scheelite crystals from an Archaean gold deposit (Mt Charlotte, Western Australia)

J. Brugger
Y. Lahaye
D. D. Lambert

VIEPS, Department of Earth Sciences, Monash University,
Clayton, Victoria 3168, Australia

R. Bateman

Kalgoorlie Consolidated Gold Mines, PMB 27, Kalgoorlie, WA
6430, Australia

R. Maas

VIEPS, School of Earth Sciences, La Trobe University, Bundoora,
Victoria 3083, Australia

S. Costa

VIEPS, Department of Earth Sciences, Monash University,
Clayton, Victoria 3168, Australia

Scheelite (CaWO_4) is a widespread accessory mineral in mesothermal Au deposits of various ages. Scheelite can host relatively large amounts of Sr and *REE* (up to > 1 wt.% *REE*), and has been used to date mineralisation, and to constrain the nature and origin of the ore-forming fluids (Anglin *et al.*, 1996; Eichhorn *et al.*, 1997; Kent *et al.*, 1996; Müller *et al.*, 1991).

The Archaean Yilgarn Craton (Western Australia) consists of large volumes of felsic basement supporting relatively thin (< 8 km) greenstone belts. Many large Au deposits were formed in the greenstone belts of the Eastern Goldfields Province during a major crustal scale mineralising event at around 2.63 Ga. The Mt Charlotte deposit is a large quartz stockwork embedded in a differentiated gabbroic sill (locally known as 'Golden Mile Dolerite') within the Norseman-Wiluna greenstone belt, and is spatially associated with the giant shear-hosted Golden Mile deposit (Clout *et al.*, 1990). Previous Sm-Nd isotopic studies on scheelite from Mt Charlotte (Kent *et al.*, 1996) have revealed large variations in *REE* concentrations and in $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (~ 0.2 to 0.4). The Sm-Nd data define an errorchron at 2772 ± 86 Ma, older than the mineralising event (2.63 Ga).

We present *in situ* trace element data obtained by UV laser ablation high-resolution inductively-coupled plasma mass-spectrometry (LA-HR-ICP-MS, using a Merchantek LUV266 laser microprobe and a Finnigan MAT *ELEMENT*) on scheelite from Mt Charlotte, with the aim to decipher the nature of the inhomogeneous distribution of *REE* in scheelite. The morphology of the *REE* zoning in scheelite was

studied by optical luminescence (cathodoluminescence and proton induced luminescence). We have also analysed the Sm-Nd isotope geochemistry of the same zones studied by LA-HR-ICP-MS and luminescence using a micro-drilling/sampling technique.

Results

The scheelite from Mt Charlotte is Mo-free (= 5 ppm Mo), has generally high Sr contents (up to 4300 ppm), and is characterised by very inhomogeneous *REE* contents within single grains. Two types of *REE* patterns coexist in most scheelites (Fig. 1b): *MREE* enriched (hump-shape) patterns with no or a slightly positive Eu anomaly (type I), and flat or middle *REE* (*MREE*) depleted patterns with a large positive Eu-anomaly (type II).

The luminescence spectrum of scheelite is characterised by a broad band centered at 430 nm, which is responsible for the blue luminescence of Mo-free scheelite, and to which sharp peaks related to *REE*³⁺ ions are superimposed. Thus, in *REE*-rich, Mo-free scheelite, the luminescence colour can be shifted from blue to yellow.

Two types of zonation have been recognised in the scheelite from Mt Charlotte:

(1) In some crystals, luminescence reveals a *first order* oscillatory zoning involving type I (yellow luminescence; dark grey in Fig. 1a) and type II *REE* patterns (blue luminescence; light grey in Fig. 1a). The zones of contrasting *REE* composition are parallel to the crystal faces, and measure from < 10 μm to 500 μm in width. Closer inspection of the zones, however, often reveals complicated fine

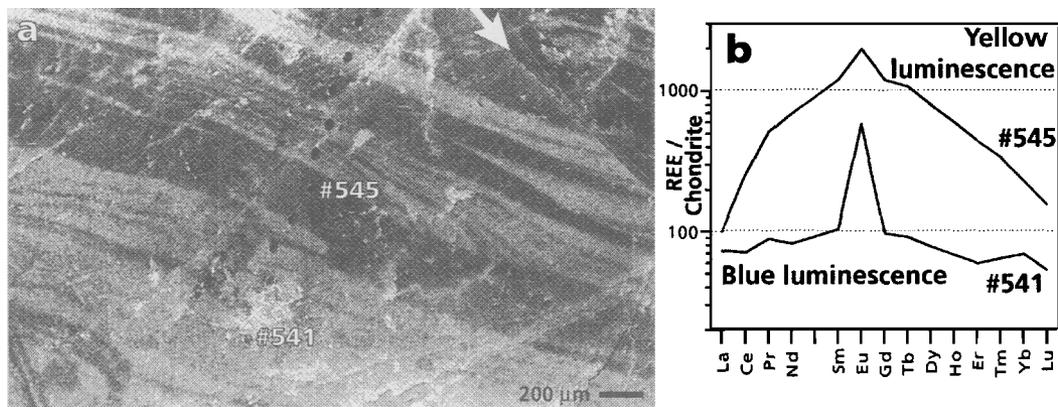


FIG. 1. *REE* zoning in scheelite from Mount Charlotte: (a) Digitally enhanced cathodoluminescence (CL) image of a zoned crystal. This 8 mm crystal displays a first order oscillatory growth zonation, but closer inspection shows complex fine structures within the zones. The arrow indicates a post-crystallisation fracture. Also note the ten ablation pits distributed across the crystal. The *REE* patterns corresponding to the two numbered ablation pits are plotted in Figure 1b. (b) The two extreme chondrite-normalised *REE* patterns among the ten analyses from the ablation pits shown in Fig. 1a.

structures, which reflect dynamic growth conditions. This growth zonation is dislocated by cracks, which formed at an unknown time after scheelite crystallisation (Fig. 1a).

(2) LA-HR-ICP-MS depth profiles (vertical resolution of 200 to 700 nm, depending on the number of analysed elements) show oscillatory zoning with zone widths = 10 μm . This *second order* zoning involves the *LREE*, and is thus different from the first order zoning which involves primarily the *MREE*.

Small but significant differences in the initial isotopic compositions of Nd exist between zones of predominantly yellow ($\epsilon\text{Nd}_{2.63} = 2.5\text{--}3.5$) and blue ($\epsilon\text{Nd}_{2.63} = 1.1\text{--}2.6$) luminescence (first order zoning).

Discussion

The oscillatory zoning involving *REE* in the Mt Charlotte scheelite is a primary feature. Where luminescence was able to map the distribution of *REE*, no evidence for post-crystallisation *REE* mobility (e.g. recrystallisation along the rim of the crystals or along cracks) has been detected. The transition from a *MREE* enriched pattern (type I) to a flat or *MREE* depleted pattern (type II) can be explained if a fluid with an originally flat *REE* pattern crystallises a mineral which preferentially incorporates *MREE*, like scheelite, for example. In this case, the increase of the Eu anomaly from type I to type II

patterns may not reflect a change in the oxidation state of Eu in the fluid, but may result from a smaller partition coefficient for Eu^{2+} relative to Eu^{3+} . Thus, Eu will be less rapidly depleted in the fluid than the other *REE*, resulting in a growing positive Eu anomaly in the fluid, which is recorded in scheelite as well. Under the conditions prevailing during scheelite formation (325–375°C, $\text{CO}_2/\text{CH}_4 \sim 1\text{--}50$), Eu^{2+} was predominant in the scheelite-forming fluid. The inhomogeneity of the initial Nd isotopic composition reflects the complex interaction between the mineralising fluid and the heterogeneous greenstone belt, and explains the erroneous (too old) age of the Sm-Nd scheelite errorchron.

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