Magmatic-to-hydrothermal crystallization in the W–Sn mineralized Mole Granite (NSW, Australia): Part II

Evolving zircon and thorite trace element chemistry

Journal Article

Author(s):

Pettke, Thomas; Audétat, Andreas; Schaltegger, Urs; [Heinrich, Christoph A.](#)

Publication date:

2005-08-05

Permanent link:

<https://doi.org/10.3929/ethz-b-000048110>

Rights / license:

[Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International](#)

Originally published in:

Chemical Geology 220(3-4), <https://doi.org/10.1016/j.chemgeo.2005.02.017>

Magmatic-to-hydrothermal crystallization in the W-Sn mineralized Mole Granite (NSW, Australia) Part II: Evolving zircon and thorite trace element chemistry

Thomas Pettke*, Andreas Audétat⁺, Urs Schaltegger[◇] and Christoph A. Heinrich*

* Isotope Geochemistry and Mineral Resources, Dept. Earth Sciences, ETH
Zentrum NO, CH-8092 Zürich, Switzerland

⁺ Institute of Mineralogy, Wilhelmstrasse 56, D-72074 Tübingen, Germany.

[◇] Département de Minéralogie, Université de Genève, Rue de Maraîchers 13, CH-
1205 Genève, Switzerland

Corresponding author: Thomas Pettke

pettke@geo.unibe.ch

Please cite as:

Pettke, T., Audetat, A., Schaltegger, U., and Heinrich, C. A., 2005. Magmatic-to-hydrothermal crystallization in the W-Sn mineralized Mole Granite (NSW, Australia) - Part II: Evolving zircon and thorite trace element chemistry.

Chemical Geology 220, 191-213.

DOI: [10.1016/j.chemgeo.2005.02.017](https://doi.org/10.1016/j.chemgeo.2005.02.017)

Abstract

The Sn-W mineralized Mole Granite in Eastern Australia hosts zircon populations that crystallized at several stages during a protracted magmatic to hydrothermal evolution. Thirty-four elements have been quantified by laser-ablation inductively-coupled-plasma mass-spectrometric microanalysis with the aim of relating the chemistry of zircon to its growth environment. Trace element contents are highly variable for all textural occurrences. Zircon inclusions in earliest quartz phenocryst suggest that zircon was a liquidus phase that crystallized probably deep in the crust. Trace element contents are conspicuously high, showing only a slight positive Ce anomaly but a pronounced negative Eu anomaly. Successive crystallization stages of magmatic zircon are characterized by progressive depletion in trace element contents, notably the rare earth elements, with an increasingly important positive Ce-anomaly. This evolution reflects saturation of REE accepting minerals such as monazite, thorite, xenotime and possibly apatite and is affected little by the exsolution of a magmatic-hydrothermal fluid. Zircon that is interpreted to have precipitated from aqueous fluids in Sn-W-bearing quartz veins shows REE patterns indistinguishable from those of late-magmatic zircon. When combined with experimental evidence on the fluid - melt partitioning of REE it indicates that the REE distribution coefficients for zircon / melt and zircon / fluid are largely comparable.

The second example of hydrothermal zircon crystallized some 2 Myrs after the host granite. These crystals reveal an intragranular zonation of increasing trace element concentrations from core to rim. Therefore, REE abundances and patterns alone are not conclusive indicators of the geological environment in which zircon crystallized. Nevertheless, variations in trace element contents of zircon that relate to the chemistry of the melt or fluid from which zircon crystallized, as measured in cogenetic melt and fluid inclusions, are promising for future petrogenetic modeling.

Lead and Cs are strongly incompatible in hydrothermal zircon, with estimated zircon-fluid distribution coefficients $D \leq 0.001$, while Sn and Li are moderately incompatible, $D_{\text{Sn}} \sim 0.6$ and $D_{\text{Li}} \sim 0.1$, and Ce is compatible, $D_{\text{Ce}} \sim 14$. Moreover,

hydrothermal zircon has a more pronounced negative Eu-anomaly and higher Ta/Nb and U/Th ratios than the magmatic zircons of the Mole Granite.

Keywords

Hydrothermal zircon, granite, trace element partitioning, Pb, LA-ICPMS

Introduction

Zircon is most widely used for U-Pb dating of magmatic events, because of its resistance to post-crystallization overprinting, which is manifested by the preservation of complex internal structures and chemical zonation patterns. The processes controlling the minor to trace element chemistry of zircon, however, are not well constrained, nor is much known how the chemistry of natural zircon may vary with the crystallization conditions, from magmatic to hydrothermal stages. Examples in the literature (e.g., Hinton and Upton, 1991; Guo et al., 1996) document variability in trace and rare earth element (REE) patterns of genetically different types of zircon, suggesting that naturally grown zircon may have distinct trace element characteristics as a function of growth environment. Recent experimental evidence, however, suggests that the incorporation of trace metals of less than 4⁺ valence into Zr^{IV}SiO₄ is limited by the ability of the zircon structure to accommodate charge-compensating elements such as P⁵⁺ (Hanchar et al., 2001; Finch et al., 2001), according to the coupled xenotime-type substitution

If directly applicable to natural zircon, these data would suggest that the trace element chemistry of zircon may generally not be useful as an indicator of provenance. Indeed, zircon crystals from a range of rock types have been reported to vary little (Hoskin and Ireland, 2000).

Among the trace elements incorporated into zircon, REE are very prominent and thus hold potential for petrogenetic modeling for cases where coeval accessory minerals such as monazite, xenotime, allanite or apatite are also considered (e.g., Condie, 1978; Hoskin et al., 2000; Poitrasson et al., 2002). While there is a fair amount of published data on REE partitioning between zircon and felsic silicate melts (e.g., Hinton and Upton, 1991, Guo et al., 1996; Thomas et al., 2002), there are only few contributions (summarized in Reed et al., 2000) dealing

with REE partitioning between an aqueous fluid and a silicate melt. No direct data exist, to our knowledge, on the trace element partitioning between an aqueous fluid and zircon at P and T relevant here. Reed et al. (2000) have demonstrated experimentally that partitioning of the REE between a peraluminous monzogranitic melt and a chlorine-bearing, sulfur- and carbon-free aqueous fluid (800 °C and 200 MPa) is strongly controlled by the total amount of Cl⁻ in the aqueous fluid phase. Rare earth elements occur as chloride complexes in the aqueous fluid, hence their concentration is dependent on the bulk salinity of the fluid. Enrichment of LREE in the aqueous fluid coexisting with silicate melt, thereby, is more pronounced than that of MREE and HREE, for all the experiments of Reed et al. (2000), consistent with results from a natural system showing a systematic enrichment in the LREE relative to the HREE in natural high-salinity fluid inclusions (80 wt-% NaCl_{equiv}; Banks et al., 1994). These observations collectively suggest that a distinct trace element signature enriched in LREE can be expected to exsolve from a silicate melt and that such a signature might characterize zircon precipitating from an aqueous hydrothermal fluid.

The possibility of hydrothermal zircon crystallization (Claoué-Long et al., 1990; Rubin et al., 1993; Kerrich and King, 1993; Kerrich and Kyser, 1994; Yeats et al., 1996; Nesbitt et al., 1999) was received with much skepticism in the literature (e.g., Corfu and Davis, 1991; Claoué-Long et al., 1992), despite extreme mobility of zirconium demonstrated for a tourmalinized granite in Cornwall (Alderton et al., 1980). Evidence for the existence of hydrothermal zircon includes petrographic criteria such as its modal abundance and the types of inclusions in zircon. Kerrich and King (1993) and Nesbitt et al. (1999) reported extreme zircon enrichment in hydrothermally altered rocks compared to the protolith, and these zircon crystals contained inclusions of aqueous fluid and ore minerals of hydrothermal origin. Rubin et al. (1993) documented the presence of hydrothermal zircon crystals in replacement bodies of fluorite in limestone. Finally, various hydrothermal experiments demonstrated the mobility of Zr in aqueous solutions (Aja et al., 1995; Watson et al., 1997) but there are hardly any Zr concentrations from natural hydrothermal fluids published up to date (two concentrations of 18 and 4 µg/g, respectively, are published in Audétat et al., 2000a).

Laser-ablation inductively-coupled-plasma-mass-spectrometry (LA-ICPMS) has made it possible to analyze - during a single ablation - major to trace element concentrations in minerals, and multiphase bulk inclusions in minerals, without the need to expose them to the sample surface, such as fluid (e.g., Günther et al., 1998, Heinrich et al., 2003) and melt (e.g., Audétat et al., 2000a; Halter et al., 2002; Pettke et al., 2004) inclusions. This paper attempts to characterize the major to trace element chemistry of zircon and coexisting thorite grown during progressive melt fractionation from magmatic up to, and including, hydrothermal crystallization, based on the example of the Sn-W mineralized Mole Granite in Eastern Australia. It was anticipated that there could be a set of trace elements (including REE) that could unequivocally fingerprint crystallization of zircon from an aqueous hydrothermal fluid. We hypothesize about the response of hydrothermally grown zircon on the complex fluid compositions of natural systems (based on fluid inclusion chemical data by Audétat et al., 1998, 2000a,b). The data set presented here is part of a larger effort to better characterize the chemistry of accessory minerals that crystallized during the magmatic-hydrothermal transition of a crystallizing pluton and associated magmatic-hydrothermal mineralization. Uranium-lead age data on magmatic and hydrothermal zircon, monazite and xenotime, and complementing trace element chemistry are discussed in the companion paper of Schaltegger et al. (2005).

The Sn-W mineralized Mole Granite

The Mole Granite belongs to a series of late leucogranites that are part of the large New England Batholith (Fig. 1 in Schaltegger et al., 2005; see also Audétat et al., 2000a,b) emplaced between 270 and 225 Ma along an Andean-type continental margin on the east coast of Australia (e.g., Flood and Aitchison, 1993). This granite is geochemically and mineralogically very homogeneous at the level of exposure (Audétat, 1999), despite the existence of three distinct textural variants. The pluton has a porphyritic 10-100 m thick carapace, and the main body of the intrusion is composed of seriate granite. Both rock types are cut by dikes and irregular masses of microgranite (Audétat et al., 2000a). More than 1200 small ore deposits occur within the intrusion and the overlying country rocks, and most of them have been mined for either Sn, W or base metals (e.g., Henley et al.,

1999). Some of these hydrothermal ore veins contain free-grown hydrothermal quartz in open cavities that host a variety of mineral inclusions including zircon, thorite, potassium feldspar, ilmenite, topaz, monazite, fluorite, biotite, beryl, helvite ($\text{Mn}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$), sulfide minerals, muscovite, tourmaline and cassiterite. The hydrothermal minerals precipitated from an aqueous magmatic fluid (coexisting brine and vapor) upon cooling and progressive dilution by meteoric water (Audétat et al., 1998; Audétat, 2000b).

Sample localities and description

Zircon, thorite and a few monazite crystals from fresh and hydrothermally affected granite and from free-grown hydrothermal quartz of Sn-W ore veins were analyzed for their major to trace element contents. In order to minimize the possibility of multiphase crystallization, recrystallization or hydrothermal overprinting associated with Sn-W mineralization, we analyzed only crystals occurring as inclusions in single quartz crystals of either magmatic or hydrothermal origin (Fig. 1). Crystals in the rock matrix were disregarded here. Zircon inclusions in quartz are often clear and commonly up to 60 μm in size. Thorite inclusions are transparent brown crystals that are morphologically identical to zircon (i.e., tetragonal) but often produce a conspicuous brown halo in the surrounding quartz. Monazite entirely included in quartz phenocrysts is microscopically indistinguishable from zircon and occurs only rarely.

Petrographic and age criteria were used to distinguish four different groups of zircon, thorite, and monazite samples according to their stage of crystallization. These are: (1) early magmatic; (2) late magmatic; (3) hydrothermal zircon; and (4) zircon associated with biotite-dominated hydrothermal alteration that postdates the crystallization of the host granite by ca. 2 Myrs (Schaltegger et al., 2005). These four groups are now described in detail.

(1) Early magmatic zircon was sampled from quartz phenocrysts of a macroscopically unaltered porphyritic granite (sample "vnlt" from locality Pheno, coordinates: GR 360.9E/6765.9N). Phenocrysts are equal proportions of quartz and potassium feldspar with subordinate plagioclase and traces of biotite hosted in a mineralogically identical groundmass of sub-millimeter grain size. Accessory minerals include zircon, apatite, monazite, ilmenite, topaz and fluorite, of which

zircon, apatite, and ilmenite were found as inclusions in quartz phenocrysts. Judging from the presence of ca. 40 vol% of phenocrysts in this rock, zircon inclusions in the phenocrysts are expected to have crystallized early in the magma, suggesting that zircon was a liquidus phase (compare Watson, 1979). Cathodoluminescence (CL) images for this type of zircon (Fig. 2a) reveal an early magmatic low-luminescent core termed growth Stage A, which is overgrown by oscillatory zoned zircon of magmatic growth Stage B. Growth of this early stage is dated at 247.6 ± 0.4 Ma, by U/Pb on abraded zircon crystals (Schaltegger et al., 2005).

(2) Early to late magmatic zircon co-existing with brown thorite and clear monazite as inclusions in phenocrystic quartz was sampled from a seriate granite (sample "Yank 8.1E" from the Kathida mine, Yankee Lodes, coordinates: GR 351.5E/6759.9N). Seriate granite contains the same mineralogy as the early magmatic porphyritic granite described above, but is characterized by a more uniform grain size distribution. Quartz phenocrysts host zircon, thorite, monazite, xenotime, feldspar, biotite, topaz, fluorite and crystallized melt inclusions in primary growth zones. Partial replacement of potassium feldspar in the matrix by sericite suggests some hydrothermal overprinting of this sample, likely to be associated with the nearby Sn-W-quartz mineralization. Sector zoning, corresponding to growth Stage B, is observed in CL for zircon crystals cut perpendicular to their c-axis (Fig. 2b). A few grains show a somewhat higher luminescent rim that is darker in a back-scattered electron (BSE) image (Stage B1) and apparently cuts the magmatic oscillatory growth zonation in some instances (Fig. 2b,c). These features probably result from interaction of zircon inclusions with hydrothermal fluids invading the quartz phenocrysts along cracks (as evidenced by some secondary fluid inclusions). The CL image for the Yankee Lodes zircon shown by Schaltegger et al. (2005; their Fig. 2c) has a dark CL rim that was not observed for zircon inclusions in quartz crystals analyzed here. This suggests that crystals of zircon included in quartz and in the rock matrix underwent somewhat different histories during and possibly after crystallization. The growth stages of zircon, thorite and monazite inclusions in quartz cannot be texturally related to the crystallization history of the seriate granite, but at least some of the zircon and thorite crystals are likely to have grown late in the crystallization history

of this rock. Therefore, zircon and thorite inclusions analyzed from this sample are likely to cover a larger crystallization interval than those from the porphyritic granite "vnlt". The monazite age of 247.7 ± 0.5 Ma is interpreted to be equivalent to zircon Stage B crystallization; hence, these two zircon growth stages appear coeval (Schaltegger et al., 2005).

(3) Hydrothermal zircon and thorite from samples "Yank 7" and "Yank 20" are hosted by cm-sized hydrothermal quartz crystals sampled from open vein cavities at the Kathida tin mine, Yankee Lodes (coordinates: GR 351.5E/6759.9N). The small zircon crystals (commonly between 10 and 25 μ) occur on primary quartz growth zones that predate the bulk of cassiterite precipitation. Among these, one growth zone is particularly enriched in zircon and thorite crystals (cf. Audétat et al., 2000a, their Fig. 8). Fluid inclusion data indicate that this zircon coexisted with a magmatic fluid at about 600 °C, 9 MPa, and that this fluid was characterized by elevated contents of F, Sn, and W (Audétat et al., 2000a,b). Zircon and thorite crystals are often isometric, multifaceted and aggregated to clusters comprising a few individual crystals (Fig. 1). This crystal shape closely resembles the descriptions of hydrothermal zircon associated with mesothermal gold lodes in the Abitibi Greenstone Belt in Canada (Claoué-Long et al., 1990). Tension cracks in the quartz host surrounding the crystals are often observed. Some of the crystals show a "spongy appearance", caused by the presence of numerous fluid inclusions. Other inclusions are thorite, potassium feldspar, opaque phases, and possibly xenotime. Potassium feldspar is sometimes directly attached to the zircon and thorite crystals. Apatite was never observed. Cathodoluminescence images reveal variable features for these zircon crystals. Rare, large grains (not shown in Fig. 2) reveal a core of oscillatory zonation (tentatively identified as growth Stage B), discordantly overgrown by a high-luminescent rim, itself overgrown by a thin margin that is zoned parallel to the crystal surfaces. Such crystals may represent inherited magmatic zircon. Most grains (Figs. 2d,e) depict luminescent lobe-like, internally zoned, irregular patches alternating with virtually non-luminescent patches that do not correlate with crystal surfaces, and are together defined as hydrothermal growth Stage D. The combined evidence of the presence of zircon and thorite crystals as primary inclusions in hydrothermal quartz, their multifaceted crystal shape, their peculiar CL characteristics and the presence of fluid inclusions

suggests that hydrothermal zircon and thorite indeed precipitated from the aqueous hydrothermal fluid that generated the Sn-W mineralization in the Mole Granite. This stage of zircon crystallization, intimately associated with solidification of the Mole Granite is dated at 246.2 ± 0.5 Ma by hydrothermal xenotime (zircon did not provide a precise age; see Schaltegger et al., 2005).

(4) Zircon associated with biotite-dominated alteration zones crossing the granite was collected at the Paradise Lode (coordinates: GR 358.8E/6758.9N), a Sn and W-mineralized vein of 700m length cutting through both seriate and porphyritic granite. A metasomatic biotite alteration selvage up to 30 cm thick envelops the southern end of the vein. This black rock is composed of ca. 90 vol% biotite, 4 vol% fluorite, and 2 vol% each of topaz, zircon and monazite. Zircon (up to 500 μm long), monazite and topaz occur as inclusions in the larger biotite grains, and the zircon crystals are surrounded by a distinctive black halo. Zircon is much more abundant in the alteration halo than in the granite, indicating its metasomatic genesis by zirconium addition to the rock (compare Nesbitt et al., 1999). Cathodoluminescence images (Fig. 2f) generally reveal a core of regular oscillatory zonation, followed by a variably thick low-luminescent rim cutting the oscillatory growth zonation. U-Pb isotope geochemistry of this zircon indicates partial lead loss, hence no precise age could be obtained. Associated monazite interpreted to be of hydrothermal origin yields a concordant U-Pb date of 244.4 ± 1.4 Ma, postdating the solidification of the host granite by about 2 Myrs (Schaltegger et al., 2005).

Analytical methods

Zircon and thorite crystals were analyzed for their major to trace element chemistry by LA-ICPMS, with an emphasis on the petrographic control of the relative succession of mineral crystallization presented above. Inclusions in quartz were analyzed in bulk, while spot analysis (core and rim) was done on the larger exposed crystals from the Paradise lode. The advantage of analyzing quartz-hosted zircon inclusions is twofold. Firstly, it allows for a better resolution of the relative growth history of zircon in a crystallizing magma according to the entrapment sequence; and secondly, inclusions are better shielded from post-crystallization modifications such as hydrothermal overprinting, and

metamictization cannot induce selective element losses (e.g., radiogenic Pb) through the host phenocryst.

Our LA-ICPMS setup consists of a pulsed 193 nm ArF Excimer laser (Lambda Physik, Germany) with a homogenized beam profile (Microlas, Germany) interfaced to an ELAN 6100 (Perkin Elmer, Canada) ICPMS (Günther et al., 1997). Machine parameters are summarized in Table 1, and details on the analytical procedure can be found in Pettke et al. (2004). Data reduction was done using LAMTRACE and in-house spreadsheets following methods described by Heinrich et al. (2003) and Halter et al. (2002). Bracketing external standardization was done on the certified SRM 610 silicate glass from the National Institute of Standards and Technology.

Internal standardization of the analyses is required to correct for differences in laser ablation efficiency between NBS 610 and the samples. This was done as follows. Ablation of an inclusion produces a signal consisting of a mixture of inclusion and host quartz evolving in unknown proportions with time (Fig. 3). These transient analyte signals were quantified via internal standardization to a total of 67.2 wt-% element oxides, i.e., 100 wt-% element oxides minus the stoichiometric SiO₂ content of the zircon of 32.8 wt-%. This approach assumes that element contents in the quartz other than SiO₂ do not contribute significantly to the zircon inclusion signal. The approach of using the total of element oxides to determine the relative sensitivity factor was evaluated by Leach and Hieftie (2000). They concluded that it is viable as long as all the elements significantly contributing to the total have been analyzed reliably. For the data set presented here, this is the case except for P₂O₅ that was not always analyzed, and Si, which cannot be reliably quantified due to the dominant host quartz contribution. For quantification, a concentration value thus had to be assigned to these two elements, which fortunately share the same site in the crystal structure of zircon for the common case where incorporation of REE is dominantly by coupled xenotime-type substitution (Speer, 1982). Concentrations of SiO₂ in zircon reported in the literature are usually between 27 and 33 wt-%, those of P₂O₅ in synthetic runs never exceed 5 wt-% (e.g., Hanchar et al., 2001). The composition of thorite was quantified accordingly to a total of 81 wt-% element oxides (i.e. 100 wt-% – stoichiometric SiO₂). Monazite chemistry was quantified by normalizing to

80 wt-% element oxides (i.e., 100 – 20 wt-% P_2O_5 ; average of 14 analyses in Schaltegger et al., 2005). The major contribution to the total uncertainty on the absolute element concentrations thus arises from the internal standardization. Our conservative estimate of the total uncertainty is $\pm 5\%$ except where the analytical precision was limited by counting statistics for elements analyzed close to their limits of detection (LOD). This analytical uncertainty is rather large for major elements such as ZrO_2 , but compares well with uncertainties inherent in other microbeam techniques (e.g., Secondary Ion Mass Spectrometry; Hoskin, 1998).

In a second step, this mixed analyte signal was corrected for trace element contribution from the host quartz, based on the total Si signal from the inclusion plus host quartz interval. Only Li, Al, P, Sn and Bi are present in the quartz at significant concentration levels relative to zircon, thorite and monazite (17 $\mu\text{g/g}$ Li, 150 $\mu\text{g/g}$ Al, 20 $\mu\text{g/g}$ P, 26 $\mu\text{g/g}$ Sn and 0.04 $\mu\text{g/g}$ Bi on average; Table 2). Because the signal interval of the zircon inclusion was sometimes associated with a dominant quartz signal contribution (i.e., the mass of inclusion divided by the total mass ablated was often < 0.2), the concentrations of Li, Sn and Bi in zircon and thorite may have uncertainties of up to $\pm 50\%$ in the worst case.

Limits of detection were calculated for each element and analysis individually as three times the standard deviation of the background signal (taken before laser ablation) divided by element sensitivity during the respective ablation. For non-significant analyte signals, LOD values are reported in Tables 2 and 3, marked by $<\text{LOD}$. The smaller the inclusions are (i.e., the smaller the chosen pit size was), the higher the resulting LOD will be for a given element since the background signal remains the same while the amount of mass ablated per unit time decreases roughly by the square of the radius of the pit size. This only applies in such a predictable way for laser systems with a homogeneous energy density across the ablation pit. Additionally, pure quartz essentially dilutes the analytical signal of zircon measured as inclusions, thereby reducing the sensitivity of all elements in the zircon signal. Therefore, LODs were about a factor of 5 higher than for direct mineral analysis, so that only the minimal size of the negative Eu-anomaly (Table 3) could be determined for some zircon inclusions.

The total Pb content of some hydrothermal zircon and thorite inclusions was determined by analyzing all isotopes of Pb and summing them up. The total signal

obtained on mass 204 was strongly dominated by ^{204}Hg (estimated from $^{202}\text{Hg}/^{204}\text{Hg} = 4.35$; Rosman and Taylor, 1998), hence the ^{204}Pb concentrations in the hydrothermal zircon crystals are only known to be below $\sim 1 \mu\text{g/g}$. This translates to initial Pb concentrations of a few tens of $\mu\text{g/g}$ of Pb as an upper limit (assuming common Pb isotopic compositions). A more reliable way of estimating the initial Pb content in the present case is to subtract the in-situ growth contribution from the decay of U and Th during 247 Ma (Schaltegger et al., 2005). This way, the common Pb content was calculated to be not different from zero (permitting for 5% total analytical uncertainty on U, Th and Pb) in all cases but one, where the concentration of initial Pb resulted in $34 \mu\text{g/g}$. This analysis (m_03a15 in Table 3) is interpreted to reveal a Pb-rich fluid or mineral inclusion within the zircon grain and is thus not considered further.

It is important to understand, finally, that the method of internal standardization applies the same relative sensitivity factor to all the elements in one analysis, hence the ratios between the various elements remain unaffected by internal standardization. Therefore, element ratios in the sample are uniquely determined by the use of external standardization only. This implies that the shape of the chondrite-normalized REE patterns, for example, are insensitive to the type of internal standardization applied; internal standardization only affects the absolute concentrations of all the elements, to the same extent, within a single analysis.

Results

Measurements were recorded as raw data in time-resolved mode (Fig. 3), enabling partial resolution of small-scale chemical heterogeneities within grains such as chemical zonation between core and rim sections of the included crystal (e.g., U/Hf in Fig. 3a) or the presence of tiny inclusions not necessarily visible with a petrographic microscope (Fig. 3b). In such cases, only sections of signals corresponding to inclusion-free zones or to core or rim sections of included grains were integrated (marked as "core interval" or "rim interval" in Table 3). This has proven to be essential, because the majority of analyzed zircon grains showed signal evidence for inclusions – elevated signals of Na are characteristic for fluid inclusions, the presence of mineral or melt inclusions was revealed by Al, K_2O , Sn or Ce. Such splitting of signals does not provide pure core or rim compositions of

grains but, as shown below, chemical trends with progressive zircon crystallization are well resolved. The results for zircon and thorite analyses free from inclusion contamination are reported in Table 3.

Trace element concentrations in zircon generally decrease from early magmatic to hydrothermal zircon, except for Li, Ta and, to a lesser extent, Sn (Fig. 4a,b,c). All chondrite (McDonough and Sun, 1995) normalized REE patterns of zircon are steep and HREE-enriched. The HREE enrichments (≤ 75000 -times chondritic) in early magmatic zircon of the Yankee Lodes are exceptional, exceeding examples from the literature for gabbros to granites, ophiolites, charnokites, carbonatite and kimberlite (e.g. Hoskin and Ireland, 2000; Hoskin et al., 2000), of alkaline rocks (Hinton and Upton, 1991), of high-grade metamorphic rocks (e.g. Barbey et al., 1995; Bea, 1996, Rubatto, 2002), and even zircon of hydrothermal origin (Hoskin et al., 1998). Only zircon inclusions in corundum (Guo et al., 1996) showed similar HREE enrichments and trace element concentrations. The REE patterns show a strong negative Eu anomaly and a variably positive Ce anomaly that becomes more and more positive from early magmatic to hydrothermal zircon in the Yankee Lodes samples (Fig. 4). The steepness of the REE patterns increases from early magmatic to hydrothermal zircon, from $La_N/Lu_N \sim 3.5 \cdot 10^{-3}$ to values as low as $3 \cdot 10^{-5}$. Heavy REE and MREE enrichments are uniform throughout. The degree of LREE depletion positively correlates with the size of the positive Ce-anomaly that is most pronounced for hydrothermal zircon. Concentration plots of HfO_2/Y_2O_3 vs. ZrO_2/Y_2O_3 or Ta/Nb vs. ZrO_2/Y_2O_3 (Fig. 5) show correlations between distinctive clusters for each of the petrographic groups. A more detailed presentation of the results follows, grouped according to the petrographic types of zircon.

(1) Early magmatic zircon: sample "vnlt"

Trace element contents (Table 3) are fairly uniform and decrease conspicuously from core to rim while only ZrO_2 distinctly increases from 47 to 60 wt-%. HfO_2 remains essentially constant around 1.4 wt-%. Chondrite-normalized REE patterns are HREE-enriched and show $Yb > Lu$ where Yb is up to 75000 times chondritic (Fig. 4a). A pronounced negative Eu anomaly of ~ 0.026 is developed, while there is virtually no anomaly for Ce ($Ce/Ce^* \sim 1.2$). Thorium/uranium ratios are fairly uniform between 0.34 and 0.48 and much lower than the Th/U ratio of ca. 2.5 of

the bulk rock (Audétat, 1999), with concentrations of 0.7 to 1.4 wt-% UO_2 ; these ratios are also lower than those typical for igneous zircon (e.g., Hoskin and Schaltegger, 2003). Early magmatic zircon is characterized by low Hf/Y, Zr/Y and Ta/Nb ratios (Fig. 5).

Zircon – melt distribution coefficients calculated from averages of early magmatic zircon ($n = 4$) Mole Granite ($n = 14$) bulk rocks are provided in Table 4. Hafnium, Nb, Sn, Th, U, Y and the REE all partition in favor of zircon.

(2a) Late magmatic zircon: Yankee Lode

Strongly variable trace element contents characterize this petrographic type of zircon, and the concentrations are generally lower than those of the early magmatic zircon. The decrease of trace element contents from core to rim intervals is conspicuous. Late magmatic zircon crystals are essentially devoid of FeO and have much more uniform Y_2O_3 and ZrO_2 concentrations (around 1 and 60 wt-%, respectively; Table 3). HfO_2 tends to be elevated with respect to early magmatic zircon. Chondrite-normalized REE patterns (Fig. 4b) show $\text{Yb} \leq \text{Lu}$ where Lu is up to 32000 times chondritic. Heavy REE and MREE values vary up to one order of magnitude, while those of the LREE vary almost three orders of magnitude. The negative Eu anomaly is of the same magnitude as that of the early magmatic zircon. The positive Ce anomaly is conspicuously evolving from $\text{Ce}/\text{Ce}^* \sim 1.3$ (core intervals) to values as high as 38 (rim intervals; Table 3). Thorium/uranium ratios vary between 0.13 and 0.80, with concentrations of UO_2 varying between 0.11 and 1.76 wt-%, those of ThO_2 between 0.05 and 1.18 wt-%. In element correlation plots ($\text{HfO}_2/\text{Y}_2\text{O}_3$ vs. $\text{ZrO}_2/\text{Y}_2\text{O}_3$ or Ta/Nb vs. $\text{ZrO}_2/\text{Y}_2\text{O}_3$; Fig. 5) late magmatic zircon crystals always plot in between early magmatic and hydrothermal zircon.

(2b) Late magmatic monazite: Yankee Lode

Monazite coexisting with zircon and thorite as inclusions in quartz crystals are characterized by steep chondrite-normalized REE patterns (Fig. 4e) strongly enriched in LREE (La is up to 530000 times chondritic). They are essentially devoid of a Ce-anomaly but have a pronounced negative Eu-anomaly ($\text{Eu}/\text{Eu}^* \cong 0.005$). This pattern is closely comparable to that obtained on the monazite

separated from the rock matrix by Schaltegger et al. (2005) but somewhat steeper ($\text{La}_\text{N}/\text{Lu}_\text{N} \leq 780$). Concentrations of Y_2O_3 are between 1.1 and 1.5 wt-%, those of ThO_2 and UO_2 are variable between 15 – 30 and 0.25 – 0.51, respectively, while the ThO_2/UO_2 ratios are fairly uniform between 51 and 75. This is much higher than that found for whole monazite grains from the matrix by isotope dilution (Schaltegger et al., 2005), reflecting a conspicuously high ThO_2 content that may be characteristic for earlier crystallized monazite inclusions in quartz phenocrysts (i.e., prior to crystallization of thorite, see below). Other trace elements (Table 3) are generally below a few tens of $\mu\text{g/g}$ concentration levels.

(3) Hydrothermal zircon: Yankee Lode

Hydrothermal zircon shows overall lower trace element abundances than both magmatic types. Concentrations of Y_2O_3 are below 0.67 and Fe contents are usually below a few hundred $\mu\text{g/g}$. ZrO_2 exceeds 60 wt-%, and HfO_2 concentrations are highest in hydrothermal zircon, between 1.51 and 4.30 wt-%. P_2O_5 values are low, between 0.15 and 0.29 wt-%. Values for Sn tend to be elevated in hydrothermal zircon when compared to magmatic zircon. Chondrite-normalized REE patterns (Fig. 4c) show $\text{Yb} < \text{Lu}$ where Lu is up to 23000 times chondritic. Chondrite-normalized HREE and MREE values vary less than about a factor of 5, while those of the LREE vary somewhat more than an order of magnitude. Again, Eu was not always detected, but the extent of the negative Eu anomaly appears to be similar to that documented for the magmatic zircon populations. The positive Ce anomaly is variable between 2.7 and 18.6, with two much higher values, 39 and 45 (Table 3). Ta/Nb ratios are distinctly elevated with respect to magmatic zircon. Th/U ratios are between 0.06 and 0.28, lower than those of magmatic zircon, as are concentrations of U and Th ($0.13 < \text{UO}_2 < 0.72$ wt-%; $0.01 < \text{ThO}_2 < 0.13$ wt-%). Similarly low Th/U ratios were reported for hydrothermal zircon from massive sulfide deposits of the Iberian Pyrite Belt (Nesbitt et al., 1999).

Partition coefficients between hydrothermal zircon and hydrothermal fluid of the Yankee Lodes are provided in Table 5 for Li, Sn, Cs, Ce, Pb and Bi. Fluid compositions were determined by LA-ICPMS on pseudosecondary inclusion assemblages that start from the same primary growth zone where zircon crystals

were included. Only Ce partitions in favor of zircon. The other trace elements can be grouped into elements that are slightly incompatible (Li, Sn, Bi) and strongly incompatible (Cs and Pb) in hydrothermal zircon.

Late magmatic (2) and hydrothermal (3) thorite: Yankee Lode

Brown thorite shows markedly different REE contents and chondrite normalized patterns (Fig. 4d) when compared to those of zircon and monazite. REE contents ($0.56 \text{ wt-\%} \leq \sum_{\text{REE-oxides}} \leq 1.56 \text{ wt-\%}$) are variable and comparable to those in early magmatic zircon but show an upward convex spectrum documenting strong MREE and some HREE enrichment ($0.040 \leq \text{La}_N/\text{Dy}_N \leq 0.007$ and $0.086 \leq \text{La}_N/\text{Lu}_N \leq 0.013$, respectively). Thorium/uranium ratios are between 2.1 and 4.7. The REE patterns show a pronounced negative Eu-anomaly ($0.0232 > \text{Eu}/\text{Eu}^* > 0.0008$) and a slight positive Ce anomaly ($1.63 > \text{Ce}/\text{Ce}^* > 1.18$). Trace element patterns are indistinguishable for late-magmatic and hydrothermal thorite.

(4) Hydrothermal zircon: Paradise Lode

Crystallization of hydrothermal zircon associated with biotite-rich hydrothermal alteration at the Paradise Lode postdates the crystallization of the host granite by ca. 2 Myrs (Schaltegger et al., 2005). Paradise Lode zircon is characterized by trace element concentrations that increase by up to a factor of 50 from core to rim, opposite to the trend documented above for early magmatic to hydrothermal zircon from the Yankee Lodes. Chondrite-normalized REE patterns (Fig. 6) are HREE enriched ($\text{Lu} \leq 36000$ times chondritic) and become flatter from core to rim sections ($0.005 \geq \text{La}_N/\text{Lu}_N \geq 0.037$). Core sections have ZrO_2 and Y_2O_3 concentrations around 64.5 and 0.3 wt-%, respectively, and HfO_2 concentrations are around 1.3 wt-%. Rim sections have lower contents of ZrO_2 (~55.7 wt-%) but higher Y_2O_3 and HfO_2 (up to 2.5 and 3.5 wt-%, respectively). $\text{ZrO}_2/\text{Y}_2\text{O}_3$ ratios decrease from core to rim while Ta/Nb ratios remain uniform (Fig. 5b). Sn values are also elevated in rim relative to core zones. Thorium and U concentrations of core sections are lower than magmatic values reported above, and Th/U ratios are around 0.35. Rim sections are characterized by much higher Th and U concentrations and lower Th/U ratios that approach 0.15. The pronounced

negative Eu anomaly and the weak positive Ce anomaly are uniform for core and rim sections at about 0.07 and 1.5, respectively.

Discussion

The first and most important finding of the present study is the considerable variability of zircon trace element chemistry that relates to the stage at which zircon crystallized from a progressively evolving felsic magma and related hydrothermal fluids. The zircon chemistry appears to be highly sensitive to the physico-chemical environment in which zircon crystallized, in obvious contrast with the conclusions drawn by Hoskin and Ireland (2000). Trace element incorporation into early magmatic zircon, interpreted to have crystallized at a deep crustal level, exceeded 10 wt-% total element oxides, hence was apparently never limited by the incorporation of charge-compensating elements (cf. Hanchar et al., 2001; Finch et al., 2001). Checking for charge balance assuming that the xenotime-type substitution (eqn 1 above) dominates trace element incorporation into zircon, the molar sum of (Y and REE)³⁺ exceeds that of (P+Nb+Ta)⁵⁺ by a factor of 1.5 to 1.9 (10 out of 11 analyses where P analyses are available; Table 3), consistent with observations in both natural and synthetic occurrences (e.g., Speer, 1982; Hinton and Upton, 1991; Hanchar et al., 2001). Assuming that interstitial Li (Li⁺ = 0.60Å) accounts for charge balance of the excess (Y+REE) we find that only one zircon grain contains more Li than required for charge balance (shot m_02a16; Table 3), the other zircon grains are approaching charge neutrality (permitting for up to 50% analytical uncertainty on Li due to the often high correction for Li contributed by the host quartz) or still preserve a charge deficit. It can further be speculated that interstitial Al, Fe and possibly Mg (not analyzed) may account for charge balance in early magmatic zircon (Hoskin et al., 2000) as Al and Fe are strongly enriched (sample vnlt; Table 3). Other possibilities to obtaining charge balance include the incorporation of H⁺ or (OH)⁻ or the protonation of the O²⁻ ions of the (SiO₄)⁴⁻ groups, but our data do not allow to address these issues. The interested reader is referred to Finch and Hanchar (2003) and Hoskin and Schaltegger (2003) for a detailed summary of the current knowledge of trace element incorporation into zircon.

The extreme HREE enrichments (≤ 75000 -times chondritic) in early magmatic zircon of the Mole Granite suggests that it crystallized as the first major REE acceptor from a felsic melt that was either depleted in Eu possibly by earlier feldspar-fractionation, or it reflects an inherited source signature. The combination of zircon, monazite and xenotime U-Pb geochronology (Schaltegger et al., 2005) with the trace-element geochemistry reported here suggests that Stages A and B of zircon growth and magmatic monazite crystallization occurred at 246.7 ± 0.5 Ma during the early magma crystallization and differentiation, probably in the lower crust or during ascent of the magma, but about 1.4 Ma prior to magma emplacement in the present sill-shaped intrusion of the Mole Granite. Upper-crustal emplacement, bulk crystallization, fluid exsolution and high-temperature quartz-cassiterite mineralization are interpreted to have all occurred within a very short period near 246.2 ± 0.5 Ma. This date is recorded by hydrothermal xenotime, which precipitated from high-temperature magmatic fluids together with vein quartz and zircon crystals of Stage D, slightly before cassiterite saturation due to mixing of the magmatic fluids with meteoric water (Audétat et al., 1998, 2000). The late-magmatic zircon growth of Stage C as defined in Schaltegger et al. (2005) may be coeval with the emplacement and in-situ crystallization of the alkali feldspar granite, but neither of these two later zircon generations could be directly dated at a useful precision.

The evolution of the REE patterns of the successive zircon populations can be used as a monitor of the physico-chemical changes of the residual melt and the fluid that exsolved with progressive crystallization. The trends in the REE patterns for the Yankee Lodes (schematically shown in Fig. 7a) show an overall REE depletion from early magmatic to hydrothermal stages, most pronounced for the LREE, together with a growing positive Ce-anomaly. It monitors the successive stabilization of different sinks for REE in the magma with progressive fractionation. The progressive depletion in LREE observed for the magmatic zircon stages reflects the concurrent crystallization of monazite (Fig. 4e) and possibly apatite while the less pronounced depletion of MREE and HREE can be ascribed to growth of thorite (Fig. 4d). The exsolution of an aqueous fluid phase late in the crystallization history may provide an additional sink for REE. Reed et al. (2000) have shown experimentally (800 °C and 200 MPa) for the partitioning of REE

between a peraluminous monzogranitic melt and a Cl-bearing, S- and C-free aqueous fluid that the LREE were distributed more into the aqueous fluid than were the HREE, and that the concentrations of REE in the aqueous fluid phase increased with the total chlorine concentration in the fluid relative to those in the felsic melt. The REE pattern of a fluid is thus enriched in LREE relative to that of the coexisting silicate melt. For an aqueous fluid with a Cl^- concentration of 3.5 m, corresponding to a total salinity of ca. 20 wt-% $\text{NaCl}_{\text{equiv}}$, fluid/melt distribution coefficients were > 1 for LREE, and between 0.5 and 0.8 for HREE. The aqueous fluid in equilibrium with the residual melt in the Mole Granite had a bulk salinity of about 5wt-% $\text{NaCl}_{\text{equiv}}$ only (Audétat et al., 2000b), hence the exsolved fluid phase was most probably poorer in REE relative to the residual melt. It is therefore concluded that the REE patterns of magmatic zircon that crystallized first in absence, then in presence, of an aqueous fluid phase reflect the effects of concomitant crystallization of other accessory minerals, namely monazite, thorite and possibly apatite, and that the effect of the exsolution of an aqueous fluid was clearly subordinate.

Hydrothermal zircon crystals thus have REE patterns that are very similar to those of the late-magmatic zircon crystals (Fig. 4b,c), while the Ta/Nb ratio resolves these populations (Fig. 5). The work of Reed et al. (2000) discussed above infers that the REE signature of the magmatic-hydrothermal fluid from which the hydrothermal zircon crystals precipitated is also very similar to that of the parental silicate melt from which the fluid exsolved. This in turn suggests that the distribution coefficients of REE between zircon and an aqueous fluid are likely to be similar to those between zircon and a granitic silicate melt, implying that the REE patterns cannot resolve whether zircon crystallized from a silicic melt or from a magmatic-hydrothermal fluid derived from it. A suite of zircon populations crystallized during progressive stages in an evolving magma including associated magmatic-hydrothermal stages will thus have REE characteristics and other trace element patterns that are most prominently influenced by the co-precipitation of other REE and trace-element accepting minerals, usually accessory minerals.

The prominent positive Ce anomaly that evolves from late magmatic to hydrothermal zircon is an exception from the above rule, however. This anomaly becomes larger with progressive fractionation and likely monitors a relative

increase of Ce^{4+} in the melt and in the magmatic fluid from which zircon precipitated, suggesting an increase in f_{O_2} (compare Ballard et al., 2002). The strong preference of Ce for hydrothermal zircon relative to the aqueous fluid phase is demonstrated by its distribution coefficient, $D(\text{Ce}_{\text{zrn}}/\text{Ce}_{\text{fluid}}) \approx 14$ (Table 5), at an average Ce content of the fluid of $0.9 \mu\text{g/g}$ (Audétat, 1999). Note that the effect of coeval growth of monazite (apparently severely depleting the fluid with respect to its overall Ce content) was subordinate to that of increasing the oxidation state of the remaining Ce to Ce^{4+} , underscoring the importance of ionic radii and charge for the incorporation of trace elements into zircon.

Element distribution coefficients between zircon and hydrothermal fluid (Li, Sn, Cs, Ce, Pb, Bi ; Table 5) reveal that only Ce partitions in favor of zircon, most likely because of Ce^{4+} as outlined above. Similarly, Sn may occur both as a tetravalent or bivalent cation, where the latter appears to be important in solutions as Sn^{2+} halogen or hydroxychloro complexes (Heinrich, 1990). Incorporation of Sn into hydrothermal zircon therefore depends not only on its concentration in the solution but also on the redox state of the fluid. For Sn^{4+} (ionic radius $0.71 \text{ \AA}$), incorporation into zircon onto the Zr^{4+} site (ionic radius $0.80 \text{ \AA}$) requires no charge balance, and Sn^{4+} fits the zircon structure as opposed to Sn^{2+} (ionic radius $1.12 \text{ \AA}$).

Lead and Cs are strongly incompatible in hydrothermal zircon as could be expected from their large ion size and the lattice strain theory (e.g., Finch et al., 2001). Common Pb contents of the analyzed hydrothermal zircon (estimated from the analyzed total U-Th-Pb contents (Table 3) corrected for in-situ grown Pb since 247 Ma) do not exceed $2 \mu\text{g/g}$ for most bulk zircon analyses. With an average Pb content of the hydrothermal fluid of $\sim 2500 \mu\text{g/g}$ (Audétat, 1999), the resulting distribution coefficient $D(\text{Pb}_{\text{zrn}}/\text{Pb}_{\text{fluid}})$ is < 0.001 (Table 5), more than two orders of magnitude lower than that reported for zircon grown experimentally from Pb-rich solutions (Watson et al., 1997). Obviously, not all hydrothermally grown zircon crystals are characterized by high common Pb contents. Similarly, $D(\text{Cs}_{\text{zrn}}/\text{Cs}_{\text{fluid}})$ is also of the order of 0.001 (average fluid = $3000 \mu\text{g/g}$; Audétat, 1999). Moreover, the zircon – fluid distribution coefficients reported here should be regarded as maximum estimates - even submicroscopic fluid inclusions in the zircon with thousands of $\mu\text{g/g}$ Pb and Cs would dominate the bulk zircon Pb and Cs contents,

hence true distribution coefficients could even be much smaller than 0.001 for hydrothermal zircon.

Hydrothermal zircon from the Paradise Lode

Zircon from the metasomatic biotite selvage around the Paradise Lode reveals chondrite-normalized REE patterns that show higher REE contents for rim sections relative to its core (Figs. 6, 7b), i.e., opposite to the trends documented for Yankee Lodes zircon but closely comparable to trends reported between magmatic and hydrothermal zircon from the Boggy Plain Pluton (Hoskin et al., 1998; Fig. 7c). This demonstrates that REE patterns, by themselves, do not allow genetic inferences for zircon. Precise U-Pb zircon and monazite ages reveal that metasomatism at Paradise Lode postdates the solidification of the host Mole Granite by ca. 2 Myrs (Schaltegger et al., 2005). Zircon crystals of the Paradise Lode, therefore, cannot represent the product of simple progressive melt fractionation, fluid exsolution and hydrothermal precipitation in the shallow-crustal environment of the Mole Granite, as in the case of the Yankee Lodes zircon crystals (see above). The combined evidence of different trends in REE patterns from core to rim and the different age of these zircon crystals when compared to those of the Yankee Lode reveals that they crystallized from an independent, later fluid source of different composition that probably evolved from a hidden intrusion unrelated to the Mole Granite.

Chemical characteristics of hydrothermal zircon

A variety of sometimes contradictory statements about what is characteristic for hydrothermal zircon is dispersed in the literature (e.g., Claoué-Long et al., 1990; Rubin et al., 1993; Yeats et al., 1996; Hoskin et al., 1998; Nesbitt et al., 1999). In itself, this might suggest that not all zircon occurrences claimed to be hydrothermal in origin indeed crystallized from an aqueous fluid. However, the two contrasting examples of hydrothermal zircon shown here reveal that there is no set of chemical criteria allowing unequivocal distinction between hydrothermal and magmatic zircon (Fig. 7). Variations in trace element abundances and chondrite-normalized REE patterns are much larger for different occurrences of genetically similar zircon when compared to genetically different zircon from one occurrence,

notably for the hydrothermal environment. Findings on hydrothermal zircon from the Boggy Plain Pluton (Hoskin et al., 1998) cannot be considered universally valid. For hydrothermal zircon, the following statements may have a broader applicability and warrant more extensive testing: (1) Our estimated partition coefficients between zircon and fluid are low for Pb, hence hydrothermal zircon is not necessarily characterized by elevated common Pb contents as suggested in the literature unless such zircon crystallized from hydrothermal solutions extremely enriched in Pb (magmatic-hydrothermal fluids may contain up to 10000 $\mu\text{g/g}$ Pb); and (2) partition coefficients are higher for Li and Sn, because Li may serve as an interstitial charge-compensating element and Sn^{4+} can fit reasonably well into the Zr^{4+} site. Redox potentials evolving from magmatic to hydrothermal conditions affect the distribution coefficient of some trace elements between fluid and melt in response to changes in ionic size and charge. Elevated Ce and Sn contents (Ce^{4+} and Sn^{4+}) could thus be characteristic for hydrothermal zircon from magmatic-hydrothermal fluids, pointing to a relatively elevated oxygen fugacity.

Conclusions

Trace element chemistry data differ significantly between zircon assemblages that grew at different stages and in different chemical environments of the crystallizing Mole Granite magma and associated Sn-W-rich hydrothermal veins. Differences include absolute contents of trace elements, evolving REE patterns, extent of the negative Eu and positive Ce-anomalies and selected trace element ratios, notably Nb/Ta and Th/U ratios. This chemical variability of zircon directly reflects chemical diversity of the melt or the fluid from which the zircon precipitated. However, comparison with literature data reveals that the diversity of trace element characteristics of genetically similar zircon populations from different localities exceeds that observed between genetically different types of zircon from one locality. This is well illustrated here for zircon precipitated from hydrothermal fluids. Therefore, the trace element characteristics of zircon alone are not indicative for the magmatic versus hydrothermal origin of a given population of zircon.

Zircon may prove very useful in tracing the physico-chemical evolution with progressive crystallization, because zircon is often a liquidus phase and can

crystallize throughout the protracted magmatic to hydrothermal evolution of an intrusion. The example of the Mole Granite magma has revealed a few early zircon crystals enclosed in quartz phenocrysts highly enriched in trace elements, possibly monitoring crystallization as a liquidus phase deep in the crust. Such high trace element contents might thus be characteristic for high-pressure magmatic crystallization. Late magmatic and magmatic-hydrothermal zircon crystals are characterized by very similar REE patterns. The effect of co-crystallization of other accessory minerals, including thorite, monazite, xenotime and possibly apatite dominates in this case over the subtle differences in fractionation between zircon and the silicate melt and its coexisting hydrothermal fluid with respect to the REE. Hydrothermal fluids liberated at different stages of magma crystallization or during metamorphic devolatilization can thus be expected to have highly variable trace element contents. Zircon crystals precipitated from such diverse fluid types will thus also have variable trace element characteristics, in line with the few apparently contrasting literature data on trace element contents in hydrothermal zircon.

The following characteristics may nevertheless be generally applicable to hydrothermal zircon: (1) Distribution coefficients of Pb between aqueous fluids and zircon are very small, < 0.001 in the present case. Nevertheless, common Pb concentrations of hydrothermal zircon can be expected to vary significantly in response to strongly variable fluid Pb concentrations, e.g., magmatic-hydrothermal fluids with thousands of $\mu\text{g/g}$ Pb or mesothermal Au-forming fluids with a few $\mu\text{g/g}$ Pb only. (2) Redox conditions in the hydrothermal environment are likely to be different from those prevailing at magmatic conditions. Oxygen fugacities of magmatic-hydrothermal fluids for example are commonly higher than those in the source magma from which the fluid exsolved, hence hydrothermal zircon will be enriched in trace elements that may occur in 4^+ valence (Ce and Sn in the present case). (3) Zircon may be enriched in H^+ (not analyzed in the present study) to achieve charge balance, and this may be one of possibly few remaining general criteria for identifying zircon precipitated from hydrothermal solutions.

Acknowledgments

We appreciate the help with the cathodoluminescence work by Karsten Kunze and Marianne Landtwing. The constructive review by J. Hanchar, and the comments by an anonymous referee, helped to balance our conclusions. Support to all four authors by the Swiss National Science Foundation is acknowledged.

References

- Aja, S.U., Wood, S.A. and Williams-Jones, A.E., 1995. The aqueous geochemistry of Zr and the solubility of some Zr- bearing minerals. *Applied Geochemistry*, 10(6): 603-620.
- Alderton, D.H.M., Pearce, J.A. and Potts, P.J., 1980. Rare-earth element mobility during granite alteration - evidence from southwest England. *Earth and Planetary Science Letters*, 49(1): 149-165.
- Audétat, A., 1999. The magmatic-hydrothermal evolution of the Sn/W-mineralized Mole Granite (Eastern Australia). PhD thesis, ETH Zurich: Nr.13168.
- Audétat, A., Günther, D. and Heinrich, C.A., 1998. Formation of a magmatic-hydrothermal ore deposit: Insights with LA-ICP-MS analysis of fluid inclusions. *Science*, 279(5359): 2091-2094.
- Audétat, A., Günther, D. and Heinrich, C.A., 2000a. Magmatic-hydrothermal evolution in a fractionating granite: A microchemical study of the Sn-W-F-mineralized Mole Granite (Australia). *Geochimica et Cosmochimica Acta*, 64(19): 3373-3393.
- Audétat, A., Günther, D. and Heinrich, C.A., 2000b. Causes for large-scale metal zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Economic Geology*, 95(8): 1563-1581.
- Ballard, J.R., Palin, J.M. and Campbell, I.H., 2002. Relative oxidation states of magmas inferred from Ce(IV)/Ce(III) in zircon: application to porphyry copper deposits of northern Chile. *Contributions to Mineralogy and Petrology*, 144(3): 347-364.
- Banks, D.A., Yardley, B.W.D., Campbell, A.R. and Jarvis, K.E., 1994. REE composition of an aqueous magmatic fluid - a fluid inclusion study from the Capitan Pluton, New-Mexico, USA. *Chemical Geology*, 113(3-4): 259-272.
- Barbey, P., Alle, P., Brouand, M. and Albarede, F., 1995. Rare-earth patterns in zircons from the Manaslu Granite and Tibetan slab migmatites (Himalaya) - insights in the origin and evolution of a crustally-derived granite magma. *Chemical Geology*, 125(1-2): 1-17.

- Bea, F., 1996. Residence of REE, Y, Th and U in granites and crustal protoliths; Implications for the chemistry of crustal melts. *Journal of Petrology*, 37(3): 521-552.
- Claoué-Long, J.C., King, R.W. and Kerrich, R., 1990. Archean hydrothermal zircon in the Abitibi Greenstone-Belt - constraints on the timing of gold mineralization. *Earth and Planetary Science Letters*, 98(1): 109-128.
- Claoué-Long, J.C., King, R.W. and Kerrich, R., 1992. Reply to comment by F. Corfu and D.W. Davis on "Archean hydrothermal zircon in the Abitibi greenstone belt: constraints on the timing of gold mineralization". *Earth and Planetary Science Letters*, 109: 601-609.
- Condie, K.C., 1978. Geochemistry of Proterozoic granitic plutons from New-Mexico, US. *Chemical Geology*, 21(1-2): 131-149.
- Corfu, F. and Davis, D.W., 1991. Comment on "Archean hydrothermal zircon in the Abitibi greenstone belt: constraints on the timing of gold mineralization" by J.C. Claoué-Long, R.W. King and R. Kerrich. *Earth and Planetary Science Letters*, 104: 545-552.
- Finch, R.J. and Hanchar, J.M., 2003. Structure and chemistry of zircon and zircon-group minerals. *In Zircon* (eds Hanchar, J.M. and Hoskin P.W.O.). *Reviews in Mineralogy and Geochemistry*, 53, 1-25.
- Finch, R.J., Hanchar, J.M., Hoskin, P.W.O. and Burns, P.C., 2001. Rare-earth elements in synthetic zircon: Part 2. A single-crystal X-ray study of xenotime substitution. *American Mineralogist*, 86(5-6): 681-689.
- Flood P. G. and Aitchison J. C. (1993) Recent advances in understanding the geological development of the New England Province of the New England Orogen. *In: New England Orogen NEO'93 Conference Proceedings* (eds. Flood P. G. and Aitchison J. C.), University of New England, pp. 61-67.
- Günther, D., Frischknecht, R., Heinrich, C.A. and Kahlert, H.J., 1997. Capabilities of an Argon Fluoride 193 nm excimer laser for laser ablation inductively coupled plasma mass spectrometry microanalysis of geological materials. *Journal of Analytical Atomic Spectrometry*, 12(9): 939-944.

- Günther, D., Audétat, A., Frischknecht, R. and Heinrich, C.A., 1998. Quantitative analysis of major, minor and trace elements in fluid inclusions using laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 13(4): 263-270.
- Guo, J.F., Oreilly, S.Y. and Griffin, W.L., 1996. Zircon inclusions in corundum megacrysts. 1. Trace element geochemistry and clues to the origin of corundum megacrysts in alkali basalts. *Geochimica et Cosmochimica Acta*, 60(13): 2347-2363.
- Halter, W.E., Pettke, T., Heinrich, C.A. and Rothen-Rutishauser, B., 2002. Major to trace element analysis of melt inclusions by laser-ablation ICP-MS: methods of quantification. *Chemical Geology*, 183(1-4): 63-86.
- Hanchar, J.M. et al., 2001. Rare earth elements in synthetic zircon: Part 1. Synthesis, and rare earth element and phosphorus doping. *American Mineralogist*, 86(5-6): 667-680.
- Heinrich, C.A., 1990. The chemistry of hydrothermal tin(-tungsten) ore deposition. *Economic Geology*, 85(3): 457-481.
- Heinrich, C.A. et al., 2003. Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupled-plasma mass-spectrometry. *Geochimica et Cosmochimica Acta*, 67(18): 3473-3497.
- Henley H.F., Brown R.E., and Stroud W.J. (1999) The Mole Granite - extent of mineralization and exploration potential. In: *Regional Geology, Tectonics and Metallogensis of the New England Orogen* (ed. Flood P. G.), University of New England, pp. 385-392.
- Hinton, R.W. and Upton, B.G.J., 1991. The Chemistry of zircon - variations within and between large crystals from syenite and alkali basalt xenoliths. *Geochimica et Cosmochimica Acta*, 55(11): 3287-3302.
- Hoskin, P.W.O., 1998. Minor and trace element analysis of natural zircon (ZrSiO₄) by SIMS and laser ablation ICPMS: A consideration and comparison of two broadly competitive techniques. *Journal of Trace and Microprobe Techniques*, 16(3): 301-326.

- Hoskin, P.W.O. and Ireland, T.R., 2000. Rare earth element chemistry of zircon and its use as a provenance indicator. *Geology*, 28(7): 627-630.
- Hoskin, P.W.O. and Schaltegger, U., 2003. The composition of zircon and igneous and metamorphic petrogenesis. *In* Zircon (eds Hanchar, J.M. and Hoskin P.W.O.). *Reviews in Mineralogy and Geochemistry*, 53, 27-62.
- Hoskin, P.W.O., Kinny, P.D. and Wyborn, D., 1998. Chemistry of hydrothermal zircon: Investigating timing and nature of water-rock interaction. *In*: G.B. Arehart and J.R. Hulston (editors), *Proceedings of the 9th international symposium of Water-Rock interaction*. Balkema/Rotterdam/Brookfield, Taupo, New Zealand, pp. 545-548.
- Hoskin, P.W.O., Kinny, P.D., Wyborn, D. and Chappell, B.W., 2000. Identifying accessory mineral saturation during differentiation in granitoid magmas: an integrated approach. *Journal of Petrology*, 41(9): 1365-1396.
- Kerrick, R. and King, R., 1993. Hydrothermal zircon and baddeleyite in Val-d'Or Archean mesothermal gold deposits - characteristics, compositions, and fluid-inclusion properties, with implications for timing of primary gold mineralization. *Canadian Journal of Earth Sciences*, 30(12): 2334-2351.
- Kerrick, R. and Kyser, T.K., 1994. 100 Ma timing paradox of Archean gold, Abitibi Greenstone Belt (Canada) - new evidence from U-Pb and Pb-Pb evaporation ages of hydrothermal zircons. *Geology*, 22(12): 1131-1134.
- Leach, A.M. and Hieftje, G.M., 2000. Methods for shot-to-shot normalization in laser ablation with an inductively coupled plasma time-of-flight mass spectrometer. *Journal of Analytical Atomic Spectrometry*, 15(9): 1121-1124.
- Mahood, G. and Hildreth, W., 1983. Large partition-coefficients for trace-elements in high-silica rhyolites. *Geochimica et Cosmochimica Acta*, 47(1): 11-30.
- McDonough, W.F. and Sun, S.S., 1995. The composition of the Earth. *Chemical Geology*, 120(3-4): 223-253.
- Nesbitt, R.W. et al., 1999. U-Pb dating of stockwork zircons from the eastern Iberian Pyrite Belt. *Journal of the Geological Society*, 156: 7-10.
- Pettke, T., Halter, W.E., Webster, J.D., Aigner-Torres, M. and Heinrich, C.A., 2004. Accurate quantification of melt inclusion chemistry by LA-ICPMS: A

- comparison with EMP and SIMS and advantages and possible limitations of these methods. *Lithos* 78(4), 333-361.
- Poitrasson, F., Hanchar, J.M. and Schaltegger, U., 2002. The current state and future of accessory mineral research. *Chemical Geology*, 191(1-3): 3-24.
- Reed, M.J., Candela, P.A. and Piccoli, P.M., 2000. The distribution of rare earth elements between monzogranitic melt and the aqueous volatile phase in experimental investigations at 800 degrees C and 200 MPa. *Contributions to Mineralogy and Petrology*, 140(2): 251-262.
- Rosman, K.J.R. and Taylor, P.D.P., 1998. Isotopic compositions of the elements 1997. *Pure and Applied Chemistry*, 70(1): 217-235.
- Rubatto, D., 2002. Zircon trace element geochemistry: partitioning with garnet and the link between U-Pb ages and metamorphism. *Chemical Geology*, 184(1-2): 123-138.
- Rubin, J.N., Henry, C.D. and Price, J.G., 1993. The mobility of zirconium and other immobile elements during hydrothermal alteration. *Chemical Geology*, 110(1-3): 29-47.
- Sawka, W.N., 1988. REE and the trace element variations in accessory minerals and hornblende from the strongly zoned Mc Murry Meadows Pluton, California. *Transactions of the Royal Society of Edinburgh*, 79: 157-168.
- Schaltegger, U., Pettke, T., Audétat, A., Reusser, E. and Heinrich, C.A., 2005. Magmatic-to-hydrothermal crystallization of zircon and REE-phosphates in the Sn-W mineralized Mole Granite (NSW, Australia) over three million years – a geochemical and geochronological study. *Chemical Geology*, this volume.
- Speer, J.A., 1982. The actinide orthosilicates. In: P.H. Ribbe (editor), *Reviews in Mineralogy - Orthosilicates*. Mineralogical Society of America, pp. 113-135.
- Thomas, J.B., Bodnar, R.J., Shimizu, N. and Sinha, A.K., 2002. Determination of zircon/melt trace element partition coefficients from SIMS analysis of melt inclusions in zircon. *Geochimica et Cosmochimica Acta*, 66(16): 2887-2901.
- Watson, E.B., 1979. Zircon saturation in felsic liquids - experimental results and applications to trace-element geochemistry. *Contributions to Mineralogy and Petrology*, 70(4): 407-419.

- Watson, E.B., Cherniak, D.J., Hanchar, J.M., Harrison, T.M. and Wark, D.A., 1997.
The incorporation of Pb into zircon. *Chemical Geology*, 141(1-2): 19-31.
- Yeats, C.J., McNaughton, N.J. and Groves, D.I., 1996. SHRIMP U-Pb
geochronological constraints on Archean volcanic- hosted massive sulfide and
lode gold mineralization at Mount Gibson, Yilgarn craton, Western Australia.
Economic Geology, 91(8): 1354-1371.

Figure Captions

Fig. 1. Photomicrographs showing typical occurrences of hydrothermal zircon as inclusions in free-grown quartz. (a) Cluster of 3 zircon grains (sample Yank 7.1), (b) cluster of 5 zircon grains and a feldspar inclusion marked by the arrow (Yank 20), (c) zircon inclusion on primary growth zone of a hydrothermal quartz crystal (sample Yank 7.1) that is cut by a trail of pseudosecondary fluid inclusions, and (d) cluster of 3 zircon and one brown thorite crystal (Yank 20). Note the multifaceted short-prismatic habit of most of the zircon crystals and the radial cracks in the host quartz crystal.

Fig. 2. Cathodoluminescence (a, b, d, e, f) and backscattered electron (c) images of zircon crystals. (a) Early magmatic zircon crystal showing a low-luminescent non-zoned core (growth Stage A), zoned overgrowth typical for magmatic zircon (growth Stage B), including a high-luminescent section and a final crystal-face-parallel, low-luminescent rim (sample vnl). (b) Late-magmatic crystal cut perpendicular to its c-axis, showing conspicuous sector zoning and magmatic zonation (growth Stage B; sample Yank 8.1c). The conspicuous marginal zone (Stage B1) cutting the magmatic zonation is visualized well in BSE mode (Fig. c). This feature, observed in a few grains, and suggests some hydrothermal alteration of the zircon inclusions. (d,e) Hydrothermal crystals showing an irregular pattern of strongly contrasting luminescence with no relationship to the crystal surfaces (growth Stage D; samples Yank 20c23 and Yank 20c42). (g) Zircon crystal from the biotite alteration selvage around the Paradise Lode, showing oscillatory growth in the core and an irregular, low-luminescent rim (sample Gadet 6.2).

Fig. 3. Transient LA-ICPMS signals of mineral inclusions in quartz crystals: (a) Hydrothermal zircon (sample Yank 20c34). Note the subtle zonation of the grain with respect to the U/Hf ratio. (b) Late-magmatic thorite (sample 8.1E). Note the inclusion of a zircon crystal peaking around 60 – 70s as monitored by the concomitant increase in Zr and Hf signals. (c) Late-magmatic monazite.

Fig.4. Chondrite-normalized REE patterns for various generations of zircon, thorite and monazite. Data are shown for bulk inclusions (solid black line), core sections (solid gray line) and rim sections (dashed black line). (a) Early

magmatic zircon, (b) late-magmatic zircon, (c) hydrothermal zircon, (d) late-magmatic and hydrothermal thorite and (e) late magmatic monazite, respectively. Note that the variation in REE patterns between late magmatic and hydrothermal thorite (Table 3) does not exceed that observed for hydrothermal thorite alone.

Fig. 5. (a) Plot $\text{HfO}_2/\text{Y}_2\text{O}_3$ vs. $\text{ZrO}_2/\text{Y}_2\text{O}_3$ showing a clear positive correlation as expected for the case where incorporation of Zr, Hf and Y in zircon is dominated by xenotime-type coupled substitution. (b) The plot of Ta/Nb vs. $\text{ZrO}_2/\text{Y}_2\text{O}_3$ shows two different trends from early to late crystallization of zircon, highlighted by gray arrows. The Paradise lode hydrothermal zircon crystals associated with biotite alteration show uniform Ta/Nb ratios with variable $\text{ZrO}_2/\text{Y}_2\text{O}_3$ while the Yankee Lodes zircon crystals reveal a clear positive correlation, suggesting that the Nb/Ta ratio may be significantly fractionated between a silicic melt and a coexisting hydrothermal fluid.

Fig. 6. Chondrite-normalized REE patterns of core and rim analyses of zircon associated with biotite alteration from the Paradise Lode. Rim analyses are conspicuously enriched in REE, opposite to the trends documented for hydrothermal zircon from Yankee Lodes.

Fig. 7. Comparison of trends in chondrite-normalized REE patterns for zircon evolving from magmatic to hydrothermal crystallization (a, Yankee Lodes), core to rim trends for zircon associated with biotite alteration (b, Paradise Lode) and literature data for magmatic and hydrothermal zircon from the Boggy Plain Pluton (c, Hoskin et al., 1998). Trends from early to late crystallization of zircon, marked by gray arrows, are opposite for genetically similar zircon populations, suggesting that REE abundances and patterns alone are not indicative of the geological environment in which zircon crystallized.

Figure 1

Figure 2

Figure 3

Figure 4abc

Figure 4de

Figure 5

Figure 6

Figure 7

Table 1: LA-ICP-MS machine and data acquisition parameters

Excimer 193 nm ArF laser Complex 110I

- Output energy	100 - 140 mJ
- Energy density on sample	of the order of 10 J/cm ²
- Pulse duration	15 ns
- Repetition rate	10 Hz
- Pit sizes	Between 8 and 80 µm
- Ablation cell	Plexiglass with anti-reflection coated silica glass window
- Cell He gas flow	0.9 - 1.1 l min ⁻¹

ELAN 6100 quadrupole ICP-MS

- Nebulizer gas flow	0.80 - 0.90 l min ⁻¹ Ar
- Auxiliary gas flow	0.75 - 0.90 l min ⁻¹ Ar
- Cool gas flow	13.0 - 15.0 l min ⁻¹ Ar
- rf power	1200 - 1300 kW
- Detector mode	Dual, 9 orders of magnitude linear dynamic range
- Quadrupole settling time	3 ms
- Detector housing vacuum	1.5 - 2.8 *10 ⁻⁵ Torr during analysis

Data acquisition parameters

- Sweeps per reading	1
- Readings per replicate	300
- Replicates	1
- Dwell time per isotope	10 ms
- Points per peak	1 per measurement
- Oxide production rate	Tuned to <0.2% ThO
- Isotopes analyzed	⁷ Li, ²³ Na, ²⁷ Al, ²⁹ Si, ³¹ P, ³⁹ K, ⁴² Ca, ⁴⁵ Sc, ⁴⁹ Ti, ⁵⁵ Mn, ⁵⁷ Fe, ⁸⁹ Y, ⁹¹ Zr, ⁹³ Nb, ¹¹⁸ Sn, ¹³³ Cs, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ¹⁴⁶ Nd, ¹⁴⁷ Sm, ¹⁵³ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁷ Er, ¹⁶⁹ Tm, ¹⁷³ Yb, ¹⁷⁵ Lu, ¹⁷⁸ Hf, ²⁰² Hg, ²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi, ²³² Th, ²³⁸ U

**Table 2: Trace element data for hydrothermal quartz hosting zircon and thorite
from the Mole Granite in Eastern Australia**

		Li	Al	SiO ₂ [#]	P ₂ O ₅	Sn	Bi
		µg/g	µg/g	wt%	µg/g	µg/g	µg/g
ap27c13	Yank 8.1E	20.1	230	99.9	na	33.8	<0.030
ap27c17	Yank 8.1E	29.4	210	99.9	na	34.5	<0.034
ap27c18	Yank 8.1E	26.5	208	99.9	na	29.3	<0.029
ap27c04	Yank 7.1	<11.5	181	99.9	na	26.5	0.047
ap27d03	Yank 7.1	14.2	100	99.9	na	28.5	0.038
m_02a03	Yank 7.1	22.1	192	99.9	17.5	23.7	<0.017
m_02a06	Yank 7.1	17.8	144	99.9	21.8	38.5	<0.019
m_02a07	Yank 7.1	14.2	137	99.9	26.2	35.9	<0.048
m_02a09	Yank 7.1	23.9	212	99.9	21.8	37.3	0.018
m_03a15	Yank 7.1	11.2	89	99.9	26.2	42.6	<0.029
m_03a16	Yank 7.1	10.9	82	99.9	13.1	28.2	0.022
ap27a11	Yank 20 A/0	14.2	178	99.9	na	8.8	0.025
ap27a13	Yank 20 A/26	11.7	112	99.9	na	10.0	0.028
ap27a14	Yank 20 A/26	10.1	109	99.9	na	8.8	0.022
ap27a03	Yank 20B1	13.7	157	99.9	na	8.0	0.064
ap27a07	Yank 20B1	17.7	176	99.9	na	7.9	0.063
ap27a08	Yank 20B1	17.1	177	99.9	na	7.4	0.062
m_03a05	Yank 20B2	14.5	151	99.9	17.5	31.8	<0.030
m_03a08	Yank 20B2	20.4	192	99.9	13.1	25.0	0.029
m_03a11	Yank 20B2	17.4	178	99.9	13.1	20.8	0.019
m_03a13	Yank 20B2	<12.4	89	99.9	<34.9	41.5	<0.041
m_02a11	Yank20E34	18.1	185	99.9	21.8	37.0	<0.016
m_02a16	Yank20E42	17.0	151	99.9	26.2	35.4	<0.064
m_02a17	Yank20E42	28.3	151	99.9	26.2	30.6	<0.064
m_02a18	Yank20E42	19.7	192	99.9	13.1	29.5	0.022
average		17	150	99.9	20	26	0.04

<value

Concentrations are below the LOD given (3 * stdev of background divided by sensitivity)

na

not analyzed

#

Internal standard element used for quantification

Table 3: Major to trace element data for magmatic and hydrothermal zircon and thorite from the Mole Granite in Eastern Australia

Zircon			Li µg/g	Na2O wt%	Al2O3 wt%	P2O5 wt%	K2O wt%	CaO wt%	Sc µg/g	TiO2 wt%	MnO wt%	FeO wt%	Y2O3 wt%	ZrO2 wt%	Nb µg/g	Sn µg/g	Cs µg/g	La µg/g	Ce µg/g
VNLT 107: Early magmatic zircon																			
ap27e05	incl	core interval	16	<0.001	1.12	na	<0.001	na	na	na	<0.001	8.327	7.55	46.8	126	29	112	225	805
ap27e05	incl	rim interval	11	<0.001	1.39	na	<0.001	na	na	na	<0.001	3.698	5.87	53.8	129	107	59	41	228
ap27e03	exp	rim interval	<13	0.015	0.68	na	0.028	na	na	na	0.053	1.787	4.26	57.5	89	24	8.2	38	184
ap27e04	exp	rim interval	<26	0.007	0.45	na	0.018	na	na	na	0.042	0.746	3.47	59.9	55	32	2.0	24	129
Yankee 8.1 E: Late magmatic zircon																			
ap27a16	incl	bulk crystal	494	0.002	<0.01	na	<0.001	na	na	na	0.002	<0.001	1.12	63.2	45	183	0.3	3.07	39
ap27a17	incl	bulk crystal	575	0.003	0.44	na	0.011	na	na	na	<0.001	0.056	0.32	65.8	7.2	131	1.0	1.80	27
ap27c17	incl	bulk crystal	1383	0.039	1.92	na	0.018	na	na	na	0.002	<0.001	1.87	61.6	68	4075	2.1	4.85	80
ap27c18	incl	bulk crystal	663	0.088	3.85	na	0.182	na	na	na	0.003	0.014	1.35	61.6	81	819	77	4.12	59
ap27b05	exp	core interval	75	0.189	0.30	na	0.011	na	na	na	0.116	0.490	1.35	62.2	129	19	24	65	246
ap27b06	exp	core interval	23	0.268	0.59	na	0.033	na	na	na	0.150	3.201	1.55	59.0	337	104	106	135	558
ap27c08	exp	core interval	2.8	0.028	0.08	na	0.012	na	na	na	0.007	0.287	1.19	63.6	89	65	6.0	53	258
ap27c14	exp	core interval	2.9	0.018	<0.01	na	0.022	na	na	na	0.005	0.193	0.47	65.2	31	49	5.0	27	147
ap27c15	exp	core interval	<3.1	0.010	0.01	na	0.006	na	na	na	0.004	0.268	0.44	65.0	47	24	1.8	19	91
ap27c16	exp	core interval	2.0	0.117	0.26	na	0.026	na	na	na	0.149	0.527	1.75	60.9	197	39	5.0	61	358
ap27a17	incl	rim interval	355	<0.002	0.27	na	<0.003	na	na	na	<0.004	<0.005	0.25	65.9	2.8	76	1.1	2.3	22
ap27b04	incl	rim interval	16	0.017	<0.01	na	0.011	na	na	na	0.001	0.006	1.22	63.2	63	<3.6	2.1	0.27	43
ap27c06	exp	rim interval	26	0.032	<0.01	na	0.005	na	na	na	0.010	0.047	0.40	65.1	36	78	5.4	<0.2	12
ap27c07	exp	rim interval	<11	0.002	<0.01	na	0.002	na	na	na	0.001	<0.001	0.36	66.3	7.0	37	0.2	1.8	27
ap27c10	exp	rim interval	307	0.006	<0.01	na	0.009	na	na	na	<0.001	0.380	0.82	64.3	18	257	0.5	2.5	39
ap27c11	exp	rim interval	<21	0.008	0.01	na	0.005	na	na	na	0.001	<0.001	0.71	64.9	29	9.4	0.4	4.2	46
ap27c13	exp	rim interval	383	0.002	<0.01	na	<0.001	na	na	na	<0.001	<0.001	0.87	64.1	32	513	<0.5	0.50	30
Hydrothermal zircon (Yankee Lodes)																			
ap27a03	Yank 20B1, incl	bulk crystal	455	<0.002	0.13	na	<0.002	na	na	na	na	<0.003	0.44	63.4	28	302	0.1	0.17	13
ap27a15	Yank20 C/34, incl	bulk crystal	108	0.050	<0.10	na	<0.001	na	na	na	na	<0.006	0.32	63.4	43	<1.3	5.2	0.75	11
m_02a06	Yank 7.1, incl	bulk crystal	109	0.003	0.13	0.22	0.003	<0.06	na	0.003	na	<0.003	0.32	62.5	33	271	2.0	0.13	8
m_02a07	Yank 7.1, incl	bulk crystal	97	0.019	0.11	0.21	0.002	<0.10	na	0.002	na	<0.001	0.36	63.4	37	183	1.8	0.67	12
m_02a12	Yank 20C42, incl	bulk crystal	86	0.028	0.14	0.25	0.028	<0.11	na	0.003	na	0.055	0.39	63.5	18	262	3.7	1.61	19
m_02a16	Yank 20C42, incl	bulk crystal	189	<0.004	0.26	0.17	<0.004	<0.43	na	0.004	na	<0.004	0.22	64.0	12	365	<0.4	<0.6	12
m_03a03	Yank 20B2, incl	bulk crystal	117	0.001	0.09	0.21	<0.001	<0.15	na	0.010	na	<0.010	0.33	63.9	21	197	0.2	0.27	5.8
m_03a05	Yank 20B2, incl	bulk crystal	104	0.016	0.16	0.28	0.002	<0.19	na	0.016	na	0.016	0.61	63.6	16	188	1.4	1.15	26
m_03a07	Yank 20B2, incl	bulk crystal	51	0.010	0.04	0.15	0.003	<0.03	na	<0.001	na	<0.001	0.24	64.3	12	54	0.2	0.37	10
m_03a08	Yank 20B2, 2 grains, incl	bulk crystal	97	0.013	0.16	0.29	0.013	<0.02	na	0.013	na	0.038	0.49	62.6	36	176	1.2	0.41	12
m_03a11	Yank 20B2, 2 grains, incl	bulk crystal	119	0.001	0.19	0.19	0.014	<0.03	na	0.014	na	0.029	0.33	63.3	30	151	0.7	0.32	8.9
m_03a15	Yank 7.1, incl	bulk crystal	75	0.419	0.93	0.15	0.081	<0.26	na	<0.001	na	0.110	0.21	62.8	20	159	15	0.49	5.6
ap27a11	Yank 20A/0, incl	core interval	26	0.047	<0.12	na	0.006	na	na	na	0.004	<0.011	0.27	61.9	47	80	4.8	0.48	9.1
ap27a12	Yank 20A/0, incl	core interval	214	0.162	0.23	na	0.014	na	na	na	0.012	0.016	0.34	61.8	58	49	12	1.18	13
ap27a14	Yank20 A/26, incl	core interval	32	0.006	<0.05	na	0.005	na	na	na	0.002	<0.002	0.69	63.6	25	100	1.9	0.13	22
ap27a15	Yank20 C/34, exp	core interval	16	0.058	<0.07	na	0.009	na	na	na	0.003	0.020	0.33	63.5	40	5.3	3.5	0.28	11
ap27a05	Yank 20B1, exp	rim interval	16	0.001	<0.01	na	<0.005	na	na	na	0.001	0.015	0.17	64.1	22	3.5	0.7	0.16	2.9
ap27a06	Yank 20B1, exp	rim interval	14	<0.002	<0.01	na	0.003	na	na	na	na	0.033	0.21	64.9	10	4.7	1.0	0.29	7.8
ap27a08	Yank 20B1, exp	rim interval	549	0.007	<0.13	na	0.002	na	na	na	na	<0.008	0.22	64.3	23	201	0.1	0.11	6.6
ap27a14	Yank20 A/26, incl	rim interval	950	0.021	<0.14	na	0.010	na	na	na	0.004	0.042	0.61	63.3	30	807	4.2	0.29	22
m_03a16	Yank 7.1, incl	rim interval	255	0.083	0.13	0.18	0.033	0.12	na	<0.002	na	0.366	0.38	63.4	23	629	5.9	<0.08	18
Gadet 6.2: Zircon associated with biotite alteration (Paradise Lode)																			
ap27f03	in Bt, exp, 20 mu pit	rim	<10	0.035	1.1	na	0.032	na	na	na	0.189	0.816	1.45	59.4	113	63	9.1	139	872
ap27f04	in Bt, exp, 20 mu pit	core	<16	0.002	0.07	na	0.003	na	na	na	0.006	0.096	0.42	64.0	16	13	0.53	12	74
ap27f05	in Bt, exp, 20 mu pit	rim	<16	0.024	0.65	na	0.014	na	na	na	0.129	0.548	1.33	61.5	76	60	4.2	93	592
ap27f06	in Bt, exp, 20 mu pit	core	<6.5	0.000	0.02	na	0.002	na	na	na	0.001	0.020	0.40	64.7	6.0	5.4	0.13	5.1	30
ap27f07	in Bt, exp, 20 mu pit	rim	<22	0.035	1.6	na	0.098	na	na	na	0.251	2.378	2.50	55.7	345	125	77	322	2064
ap27f08	in Bt, exp, 20 mu pit	core	<18	0.001	0.03	na	0.002	na	na	na	0.001	0.028	0.26	64.4	7.1	8.8	0.12	6.4	41
ap27f10	in Bt, exp, 20 mu pit	rim	<17	0.069	1.8	na	0.049	na	na	na	0.327	1.350	2.17	55.7	271	122	20	240	1711
ap27f09	in Bt, exp, 20 mu pit	core	<24	0.023	0.29	na	0.024	na	na	na	0.041	0.341	0.90	62.8	48	38	1.6	58	317
ap27f12	in Bt, exp, 20 mu pit	rim	<17	0.072	2.0	na	0.067	na	na	na	0.340	1.569	2.25	55.6	339	134	61	385	2232
ap27f11	in Bt, exp, 20 mu pit	core	<12	0.036	0.55	na	0.039	na	na	na	0.075	2.676	1.35	59.6	64	77	5.1	96	527
Thorite																			
			Li ppm	Na2O wt%	Al2O3 wt%	P2O5 wt%	K2O wt%	CaO wt%	Sc ppm	TiO2 wt%	MnO wt%	FeO wt%	Y2O3 wt%	Zr ppm	Nb ppm	Sn ppm	Cs ppm	La ppm	Ce ppm
Yankee 8.1 E: Late magmatic thorite																			
ap27b03	incl	bulk crystal	20	0.008	0.06	na	0.007	na	1.9	na	0.001	0.011	1.51	264	6.4	13	7.6	58	543
ap27b03	incl	core interval	22	0.004	0.02	na	0.004	na	0.6	na	0.001	0.012	1.52	259	5.9	5.3	3.0	55	530
ap27a18	incl	rim interval	18	0.003	0.07	na	0.015	na	1.1	na	0.001	0.013	1.79	294	8.2	5.8	12	115	681
Hydrothermal thorite																			
ap27c03	incl	bulk crystal	30	<0.001	<0.01	na	0.026	na	4.5	na	0.026	0.026	1.67	313	4.5	81	0.1	73	627
ap27c03	incl	core interval	23	<0.001	<0.01	na	<0.001	na	1.6	na	0.027	0.027	1.74	287	4.9	35	<0.1	89	751
ap27c04	incl	rim interval	86	0.036	0.09	na	<0.001	na	6.1	na	<0.001	<0.001	1.44	164	6.1	91	0.2	34	325
m_03a12	incl	bulk crystal	21	0.008	0.09	0.48	<0.008	<0.42	na	0.017	na	<0.025	0.83	59	1.0	128	<0.2	8	118
m_03a13	incl	rim interval	124	0.003	0.03	0.50	<0.002	<0.21	na	0.013	na	<0.007	0.89	14572	1.3	53	0.3	13	137

Table 3 continued

	Pr μg/g	Nd μg/g	Sm μg/g	Eu μg/g	Gd μg/g	Tb μg/g	Dy μg/g	Ho μg/g	Er μg/g	Tm μg/g	Yb μg/g	Lu μg/g	HfO2 wt%	Ta μg/g	Pb μg/g	Bi μg/g	Th μg/g	U μg/g	Ce/Ce* Chond-Norm	Eu/Eu* Chond-Norm
VNLT 107: Early magmatic zircon																				
ap27e05	134	776	639	7.1	1621	702	7298	2046	7643	1487	12456	1530	1.40	48	na	1.1	4368	12873	1.1	0.021
ap27e05	45	299	385	6.5	1053	483	5120	1480	5699	1143	10036	1233	1.44	23	na	<0.01	4205	8940	1.3	0.031
ap27e03	35	242	293	4.1	771	374	4132	1198	4576	978	8701	1057	1.47	14	na	<0.56	3375	9207	1.2	0.026
ap27e04	28	174	232	3.2	635	300	3316	977	3696	777	6678	855	1.45	13	na	0.17	3098	6523	1.2	0.026
Yankee 8.1 E: Late magmatic zircon																				
ap27a16	0.77	4.4	14	<0.33	94	48	694	299	1472	347	3463	642	2.24	37	na	<0.16	2120	10894	6.1	<0.030
ap27a17	<0.6	3.8	9.5	<0.76	34	15	213	87	389	88	812	152	1.41	4.5	na	<0.76	568	1374	>6.1	<0.137
ap27c17	1.6	9.3	27	<0.55	198	100	1321	531	2440	520	4780	844	1.65	31	na	<0.55	6491	16350	6.9	<0.024
ap27c18	1.5	9.4	16	<0.20	105	57	833	359	1816	427	4266	792	2.16	59	na	0.78	2823	15299	5.7	<0.015
ap27b05	27	121	63	0.89	178	75	975	384	1808	422	4217	688	1.77	82	na	0.26	3232	14643	1.4	0.026
ap27b06	77	375	220	5.6	403	133	1272	401	1666	392	4230	678	1.97	238	na	31	1758	13438	1.3	0.058
ap27c08	35	208	144	4.0	343	118	1185	375	1506	320	2958	475	1.75	38	na	0.04	3974	7186	1.5	0.055
ap27c14	20	112	53	1.7	107	35	382	134	580	132	1305	228	1.83	20	na	0.33	767	2991	1.5	0.070
ap27c15	9.9	55	34	1.2	89	33	371	134	601	140	1429	263	1.86	42	na	0.11	1317	3611	1.6	0.068
ap27c16	47	248	180	6.5	421	162	1709	544	2237	486	4559	705	1.81	56	na	<0.01	10940	13622	1.6	0.072
ap27a17	<0.6	3.7	4.2	<0.66	39	15	191	73	343	75	729	134	1.60	2.7	na	<0.66	484	993	>4.7	<0.164
ap27b04	0.32	3.6	13	<0.05	98	52	769	333	1665	394	3948	711	2.03	45	na	0.24	2350	12524	36	<0.004
ap27c06	0.15	1.5	5.6	<0.11	35	18	262	110	581	152	1708	328	2.09	45	na	<0.11	602	4164	>17	<0.027
ap27c07	1.5	11	12	0.22	48	21	253	100	442	96	908	159	1.32	3.3	na	<0.10	574	1282	4.0	0.028
ap27c10	0.72	5.2	12	<0.61	80	40	568	235	1093	251	2329	413	1.72	12	na	0.74	1392	6115	7.0	<0.062
ap27c11	1.8	11	15	<0.10	78	39	531	218	1030	240	2360	389	1.68	18	na	<0.10	1730	6549	4.1	<0.009
ap27c13	<0.5	5.1	9.1	<0.65	79	39	589	250	1190	281	2610	479	2.00	22	na	<0.26	1638	8224	>14	<0.078
Hydrothermal zircon (Yankee Lodes)																				
ap27a03	0.28	3.4	6.4	0.14	40	21	308	129	682	180	2033	406	2.66	108	na	<0.36	663	4315	15	0.027
ap27a15	0.20	2.0	3.6	0.05	22	13	212	103	617	186	2279	469	2.86	105	na	0.59	480	4394	6.7	0.017
m_02a06	0.22	3.1	5.2	<0.06	28	15	228	99	559	157	1906	398	3.41	153	155	<0.19	296	4330	12	<0.016
m_02a07	0.82	8.2	14	<0.15	55	21	280	109	583	152	1781	364	2.27	69	198	<0.20	1126	5466	4.0	<0.016
m_02a12	1.1	7.1	10	<0.28	44	21	279	113	574	139	1514	301	2.26	39	134	0.30	617	3649	3.6	<0.039
m_02a16	<0.4	2.3	3.0	<0.47	27	12	131	58	298	74	773	159	1.92	53	62	<0.90	381	1678	>6.2	<0.159
m_03a03	0.88	6.2	13	0.20	49	21	267	99	502	136	1540	310	2.08	107	128	<0.31	635	3474	2.9	0.024
m_03a05	0.54	5.0	10	0.34	64	29	404	169	803	180	1758	328	1.77	30	155	<0.55	1263	4235	7.9	0.041
m_03a07	0.56	5.9	9.5	<0.05	35	16	204	79	387	98	1065	208	2.17	45	78	0.05	358	2113	5.5	<0.008
m_03a08	0.53	5.9	10	0.09	52	25	351	148	774	207	2328	474	2.95	116	212	2.6	623	5289	6.5	0.012
m_03a11	0.80	8.6	13	<0.06	47	20	251	97	501	134	1556	328	2.62	96	133	0.20	579	3722	4.3	<0.007
m_03a15	0.48	4.4	5.9	0.11	23	13	167	73	409	123	1531	314	2.20	84	165	<0.15	525	3512	2.8	0.030
ap27a11	0.40	4.3	5.3	0.08	26	14	225	107	656	209	2812	608	4.46	277	na	<0.08	247	3971	5.0	0.022
ap27a12	1.2	9.5	9.4	0.05	35	18	268	122	716	220	2805	584	4.26	290	na	<0.14	391	4479	2.7	0.009
ap27a14	0.24	3.4	8.7	0.11	60	31	436	188	924	219	2191	420	2.10	46	na	<0.07	1142	5834	39	0.015
ap27a15	0.23	2.1	4.1	0.01	25	14	221	105	619	183	2197	447	2.67	92	na	<0.09	573	4248	11	0.016
ap27a05	0.11	1.3	1.9	0.16	15	8	121	55	302	91	1143	239	2.63	110	na	<0.08	95	2074	5.4	0.094
ap27a06	0.29	2.2	4.5	0.33	22	11	153	65	318	79	886	177	1.86	43	na	0.20	218	1609	6.5	0.100
ap27a08	0.08	1.0	2.6	0.14	17	9	134	59	323	90	1082	230	2.25	89	na	<0.31	236	2637	17	0.065
ap27a14	0.29	2.8	8.0	0.38	51	27	384	165	812	194	1988	381	2.29	62	na	<0.39	1047	6187	19	0.058
m_03a16	0.12	1.5	5.1	<0.10	34	17	241	106	551	138	1495	301	2.20	87	135	0.20	539	3239	>46	<0.022
Gadet 6.2: Zircon associated with biotite alteration (Paradise Lode)																				
ap27f03	138	655	347	13	738	218	1824	459	1642	350	3332	527	2.45	24	na	0.46	1383	5519	1.5	0.082
ap27f04	12	67	60	1.9	160	49	409	113	406	80	733	118	1.43	3.0	na	<0.13	303	910	1.5	0.060
ap27f05	98	483	284	10	582	177	1454	373	1316	260	2313	334	1.46	6.7	na	0.21	1270	3430	1.5	0.078
ap27f06	4.4	32	35	2.0	124	42	378	108	406	80	680	112	1.03	1.0	na	0.06	280	297	1.5	0.091
ap27f07	295	1347	692	26	1319	440	3807	948	3381	699	6285	905	1.73	71	na	4.7	4637	12025	1.6	0.083
ap27f08	5.0	30	24	1.0	78	25	233	69	270	55	501	86	1.32	2.0	na	<0.08	276	645	1.7	0.070
ap27f10	282	1374	708	28	1221	368	2910	694	2437	532	5312	868	3.35	84	na	0.15	1678	11155	1.6	0.091
ap27f09	56	296	185	5.4	410	127	1016	258	883	169	1439	224	1.41	6.1	na	<0.14	943	2097	1.3	0.060
ap27f12	353	1644	779	29	1293	385	3057	725	2471	505	4619	665	1.91	51	na	1.1	2737	19314	1.5	0.089
ap27f11	98	499	321	9.4	689	204	1584	386	1284	242	2037	314	1.36	12	na	0.21	928	3799	1.3	0.061
	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Hf ppm	Ta ppm	Pb ppm	Bi ppm	ThO2 wt%	UO2 wt%	Ce/Ce* Chond-Norm	Eu/Eu* Chond-Norm
Yankee 8.1 E: Late magmatic thorite																				
ap27b03	142	1218	992	0.38	1792	468	3423	762	2038	278	1650	186	9.4	0.18	na	0.07	54.8	22.62	1.4	0.0009
ap27b03	141	1211	980	0.34	1774	460	3397	757	2032	277	1632	186	9.1	0.14	na	0.05	54.9	22.49	1.5	0.0008
ap27a18	170	1415	1014	0.42	1815	424	2985	670	1750	221	1228	140	6.5	0.48	na	0.11	60.4	16.71	1.2	0.0009
Hydrothermal thorite																				
ap27c03	166	1475	1133	2.4	2071	455	2993	619	1524	182	990	112	6.3	<0.02	na	0.26	61.6	15.60	1.4	0.0047
ap27c03	192	1678	1182	1.1	2141	462	3085	650	1608	188	994	111	4.1	<0.02	na	<0.01	63.5	13.59	1.4	0.0021
ap27c04	100	946	936	1.8	1809	451	3183	677	1749	241	1497	175	2.5	<0.22	na	0.40	52.3	25.30	1.4	0.0043
m_03a12	40	407	423	4.5																

Table 4: Zircon - melt distribution coefficients: Mole Granite and literature data

	zircon	Mole Granite	$D (X_{\text{zircon}} / X_{\text{melt}})$	$D (X_{\text{zircon}} / X_{\text{melt}})$	$D (X_{\text{zircon}} / X_{\text{melt}})$	$D (X_{\text{zircon}} / X_{\text{melt}})$	$D (X_{\text{zircon}} / X_{\text{melt}})$
	early magmatic	bulk rock	Mole Granite	MMM Pluton	Rhyolite 1	Rhyolite 2	
	$\mu\text{g/g}$	$\mu\text{g/g}$					
	n = 4	n = 14		ref. 1	ref. 2	ref. 2	ref. 3
Li	13	55	0.2				
Y	40000	75	530				
Nb	96	9.9	10				
Sn	46	6.0	7.7				
Cs	44	24	1.8				
La	79	43	1.8	3	7	27	0.08
Ce	320	100	3.2	2	10	24	1
Pr	58	12	4.8				
Nd	360	41	8.6		5	22	0.5
Hf	12000	4.1	2900	1190	3742	2645	
Ta	23	1.8	13	5	40	55	
Th	3600	47	77	15	91	62	
U	9000	17	530	173	383	298	

ref. 1 Sawka (1988)

ref. 2 Mahood and Hildred (1983)

ref. 3 Thomas et al. (2002); data from melt inclusions host zircon pairs (n=11)

Table 5: Hydrothermal zircon - fluid distribution coefficients for the Yankee Lodes

FI-number ^{&}	FI-type	Li μg/g	Sn μg/g	Cs μg/g	Ce μg/g	Pb μg/g	Bi μg/g
112	brine	1280	32	1981	0.6	2028	7.9
113	brine	1167		2357	1.1		1.3
115	brine	1276	49	2875	0.9	2468	4.1
125	brine	1534	13	3148	1.1	2287	
126	brine	1531		3337		2941	
127	brine	1190	657	3655	0.6	2139	
128	brine	2008	216	3605		2538	
129	brine	1336	407	2522		1850	
130	brine	1367	700	2633		3098	
131	brine	1371	418	3227	0.7	2489	
132	brine	1572	747	3279	1.0	3422	
average	brine	1400	360	3000	0.9	2500	4
1 stdev	brine	200	300	500	0.2	500	3
average	Hyd. Zircon [*]	134	210	2.0	12	<2 [#]	0.3
1 stdev	Hyd. Zircon [*]	106	85	1.7	6	-	0.2
n=		12	12	11	12	10	4
D(X _{zircon} /X _{fluid})		0.1	0.6	0.001	14	<0.001	0.1

[&] data from Audétat (1999)
^{*} bulk crystal data from table 3
[#] average value of 12 common Pb estimates
 (from bulk Pb measurements corrected for in-situ growth of radiogenic Pb)