MINERALOGICAL MAGAZINE, DECEMBER 1984, VOL. 48, PP. 513-17

Unusual sector zoning in Lewisian zircons

J. F. HOFFMAN AND J. V. P. LONG

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge

ABSTRACT. An unusual form of sector zoning has been recorded in some Lewisian zircons. The sectors lie in a plane cut perpendicular to the *c*-axis and are observed as variations in the intensity of cathodoluminescence, and in trace-element concentrations. Sectors radiating from the centre of growth out to the {100} faces exhibit low-intensity cathodoluminescence and are enriched in Y and depleted in Hf and Zr. Those radiating to the {110} faces are brightly luminescent, slightly enriched in Hf and depleted in Y. X-ray diffraction data, and comparison with previous studies of zircons, suggest that the sectors vary slightly in crystallographic orientation, such that the boundaries between sectors form discontinuities in the structure.

PREVIOUS studies of zoning in zircon have been reviewed by Speer (1980). Prominent concentric growth zones are common, with grains showing variation in the intensity of colouring and both coarse and fine variations of birefringence. The concentric zones are sometimes intersected by discontinuities so as to produce an hour-glass structure which is visible in sections cut in a plane containing the *c*-axis, as described recently by Sahama (1981) and Krogh (1982). Krogh (1982) has noted the presence of high concentrations of uranium in sectors which extend from the crystal terminations to the centre of the grain. Uranium-bearing sectors of the same orientation have also been produced in synthetic zircons by Chase and Osmer (1966). The present paper describes a different type of sector zoning in zircons from the granodioritic Lewisian Tollie Gneiss, which does not appear to have been recorded previously.

Experimental. Zircons separated from a sample (Locality GR NG 831782, between Gairloch and Poolewe) are predominantly pale-pink, clear or only slightly cloudy, have very low U and Pb contents and show no apparent zoning in transmitted light. They exhibit moderate to strong cathodoluminescence which reveals remarkable zoning patterns. A second, rarer, type consists of dark red-brown, cloudy, non-luminescent grains containing significant concentrations of Pb and U.

Six of the larger grains of the first type were sectioned perpendicular to the *c*-axis and polished: selected grains were mounted in a drop of epoxy resin on a small piece of microscope slide; with the aid of a binocular microscope they were then arranged in a row with their long (*c*) axes perpendicular to a straight edge of the slide and with their terminations as nearly as possible aligned along the edge. After curing the adhesive, the slide was fixed vertically in a 25 mm diameter PTFE mould and embedded in further epoxy resin so as to form a solid cylindrical mount. Careful grinding of this mount then produced a section of all six zircons which could be polished by conventional techniques.

The average size of the mounted grains was 400×150 μm, although the sample contained many much smaller crystals. Zircon A (below) was exceptionally large ($700 \times 250 \times 400$ μm) and exhibited very pronounced sector zoning. A second (zircon B) showed similar, but less well defined, zoning over part of its polished surface. The relationship of cathodoluminescence and minor-element concentrations to the sector zoning was studied in both cases. The morphology and structure of zircon A were also investigated.

Zircon A. This crystal appears uniformly pale-pink and transparent with only a few clean, sharp, cross-cutting cracks. Examination with the scanning electron microscope indicates subhedral external morphology with well developed {100} and {110} prism forms and rounded terminations. Unambiguous verification of the crystallographic orientation was obtained from X-ray oscillation and Laue photographs. The results indicate that, using the conventional unit cell parameters, $a =$ 6.6 Å and $c = 5.98$ Å, the *a* and *b* crystallographic axes are parallel and perpendicular respectively to the dominant prism faces which are therefore {100}.

No zoning is visible with either transmitted or reflected light. Cathodoluminescence, however, reveals asymmetrical dark and light sectors radiating from the centre of growth to the {100} and {110} faces respectively. Fine-scale concentric zoning and a narrow brightly luminescent rim are also visible (fig. 1). Wavelength-dispersive electron

© *Copyright the Mineralogical Society*

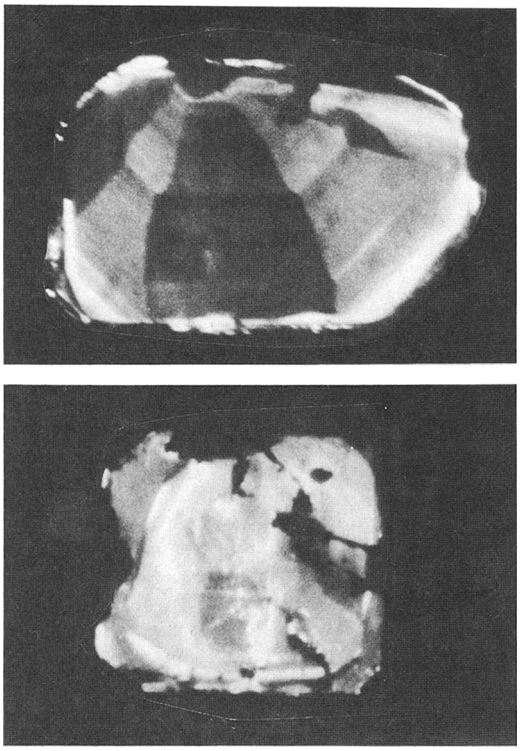

FIG. 1. Cathodoluminescence micrographs of zircons A and B.

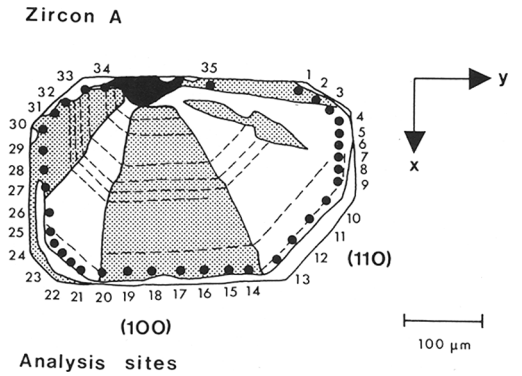

FIG. 2. Zircon A: location of sites analysed with electron probe.

microprobe analyses reveal variations in the concentrations of Zr, Hf, and Y which correlate with the sector zoning (figs. 2 and 3). Hf is enriched by ~ 15% in the light {110} sectors, whereas Y shows the reverse correlation and is enriched by a much larger factor of up to 4 in some dark sectors. Y has been recorded only as uncalibrated counts, but, by difference, cannot exceed a few percent ($ZrO_2 + HfO_2 + SiO_2$ lies between 97.8% and 99.7% for all analyses). Throughout the crystal, Zr is depleted relative to pure $ZrSiO_4$ (49.7% Zr), showing an inverse correlation with Y. Si is slightly depleted relative to pure $ZrSiO_4$ (15.3% Si), but shows no detectable systematic variation between sectors. Other elements that might be expected to have a zoned distibution, e.g. U, Pb, Fe, Ca, were, if present, below the detection limit of the electron microprobe.

There is no visible evidence, or indication from the electron microprobe analyses, that the Y is held in discrete inclusions or intergrowths, e.g. as xenotime, YPO_4. Laue photographs indicate that all sectors have essentially the same crystallographic orientation but show multiple spots, the interpretation of which is discussed below.

Zircon B. This crystal is slightly cloudy in transmitted light and featureless in reflected light, except for a few irregular cracks. Zoning patterns, revealed by its cathodoluminescence, are very irregular and complex, but sector zoning is visible in one quadrant (fig. 1). Variations in Hf and Y, from electron microprobe analyses, are similar to those in zircon A, but outside the visible sectors both elements show relatively constant plateaus of concentration (figs. 4 and 5).

Discussion. The sector zoning observed in these zircons is visible in sections cut perpendicular to the *c*-axis. Sectors radiating from the centre of growth to the {100} faces are enriched in Y, depleted in Zr and Hf, and exhibit low-intensity cathodoluminescence, while those radiating to the {110} faces are depleted in Y, slightly enriched in Hf, and exhibit higher-intensity cathodoluminescence.

On the basis of numerous reports of minor-element concentrations in zircon, Speer (1980) notes that Hf, Y, and other elements commonly vary sympathetically. The inverse correlation between Hf and Y, observed in this case, is more unusual but has previously been recorded in concentrically zoned zircons by Romans *et al.* (1975).

Y associated with zircon may be present within the zircon structure, or in inclusions, intergrowths, or overgrowths of xenotime, YPO_4, as reported by Romans *et al.* (1975) and Speer (1980). The two minerals are isostructural, with closely similar lattice parameters, but, under most geological conditions, there is a wide miscibility gap such that zircon usually contains < 3 wt.% of YPO_4 in solid solution (Speer, 1980). The low concentration of Y in these zircons is within this range of miscibility and, in the absence of any evidence of xenotime inclusions or intergrowths, is assumed to be substituting for Zr.

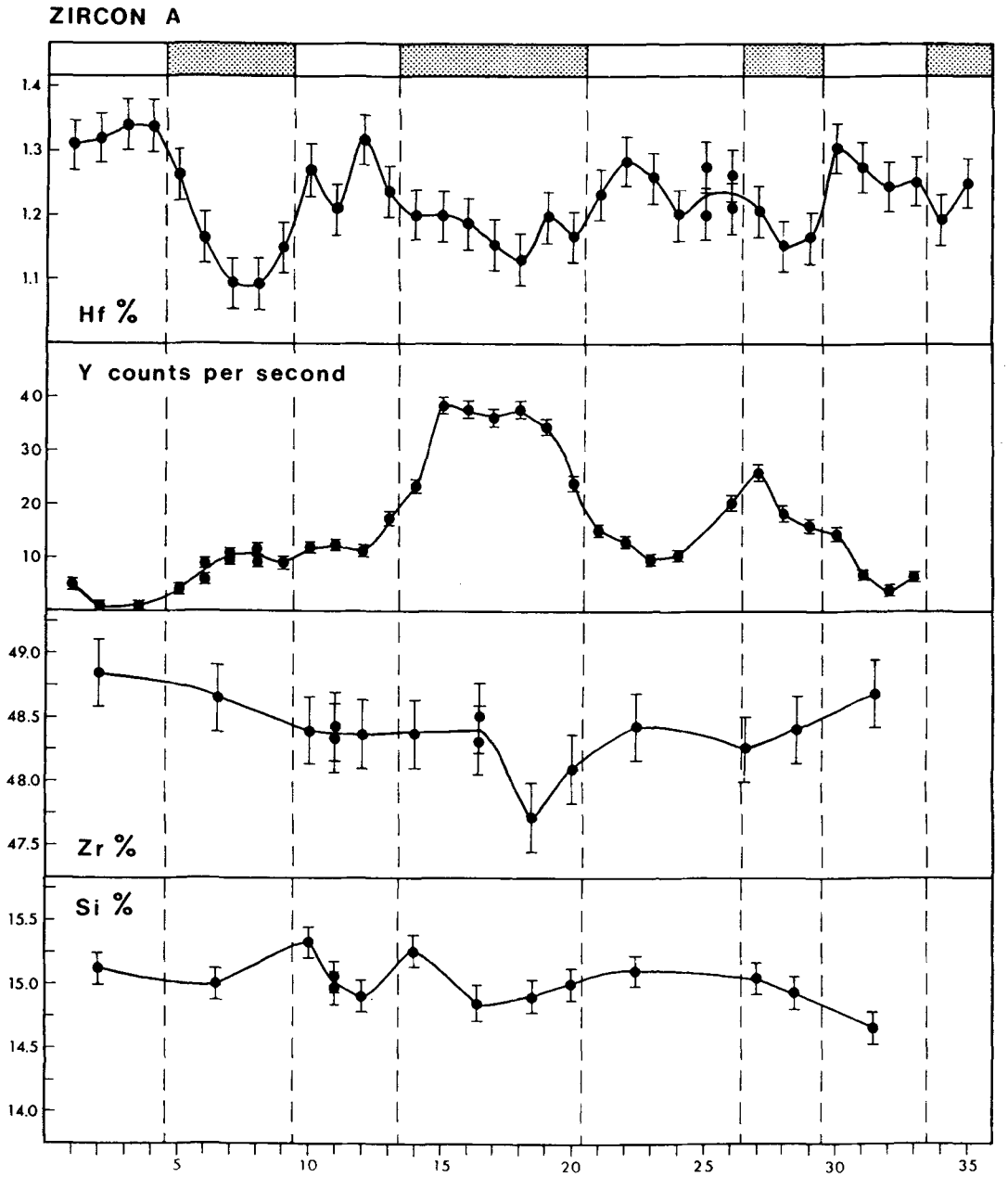

FIG. 3. Distribution of Hf, Y, Zr, and Si in zircon A. Stippled bands and numbered sites correspond to sectors and locations respectively of fig. 2.

The average Zr/Hf ratio in zircon A is 39.9, with a range of 36.9 to 44.2, close to the mean crustal value of 40. The observed range is in excess of the 2σ error, ± 2.8, resulting from counting statistics. Hf and Zr do not therefore appear to be coupled. Both elements show an apparent inverse correlation with Y, but the variation in Zr may be simply a passive response to the combined total variation of Hf, Y, and other undetected minor elements.

The relationship between cathodoluminescence and trace element content is in close agreement

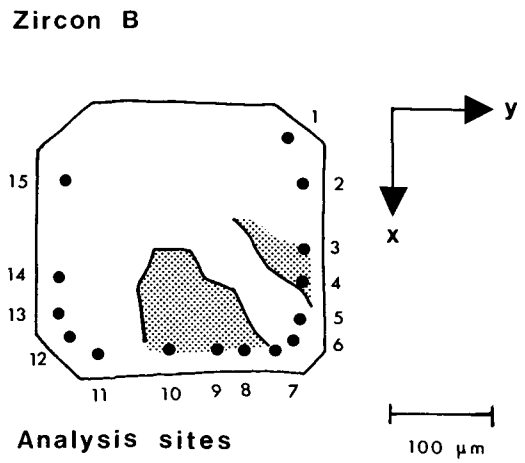

FIG. 4. Zircon B: location of sites analysed with electron probe.

with that observed by other workers. Concentrically zoned zircons described by Romans *et al.* (1975) exhibit blue cathodoluminescence which is suppressed in bands in which Y and P are enriched by a factor of 3, as compared with the surrounding luminescent zircon. The enrichment factor for Y observed in the non-luminescent sectors in the zircons studied in this case is of the same order of magnitude. Oberli *et al.* (1981) also describe zircons in which domains enriched in minor elements exhibit low-intensity cathodoluminescence compared to regions depleted in these constituents.

The multiple spots observed in the Laue photographs of zircon A can be interpreted as being due to the presence within the crystal of regions with either slightly different crystallographic orientation, or slightly different lattice parameters. In both cases obvious candidates for these regions are the observed sectors.

Effects of trace-element concentration on the lattice parameters of zircon were described by Köppel and Grünenfelder (1971) and Köppel and Sommerauer (1974). They observed evidence of two coexisting phases in X-ray powder diffraction photographs of zircons, interpreted as due to the presence of trace-element-rich domains, with slightly larger lattice parameters, within trace-element-poor host zircon. Köppel and Grünenfelder (1971) list lattice parameters of $a = 6.616$, $c = 5.999$ Å and $a = 6.643$, $c = 6.025$ Å for the two phases, with $(U+Y+Ca+P) < 0.5\%$ and 2–3% respectively. These values lie on a line between pure and metamict zircon (fig. 6) with approximately equal enlargements of a and c, which are much greater than those attributable solely to the incorporation of a total of 2–3% $(U+Y+Ca+P)$. It is probable, therefore, that the dominant cause is not expansion of the lattice by 'foreign' ions with ionic radii larger than Zr (Zr = 0.84, U = 1.00, Y = 1.02 Å), but structural damage caused by the

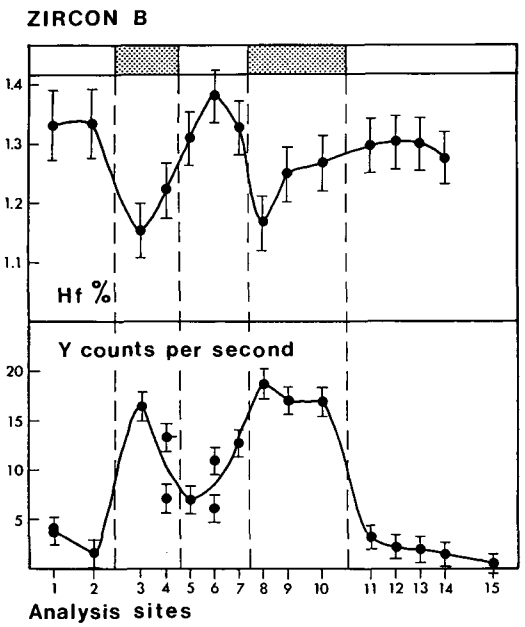

FIG. 5. Distribution of Hf and Y in zircon B. Stippled bands and numbered sites correspond to sectors and locations respectively of fig. 4.

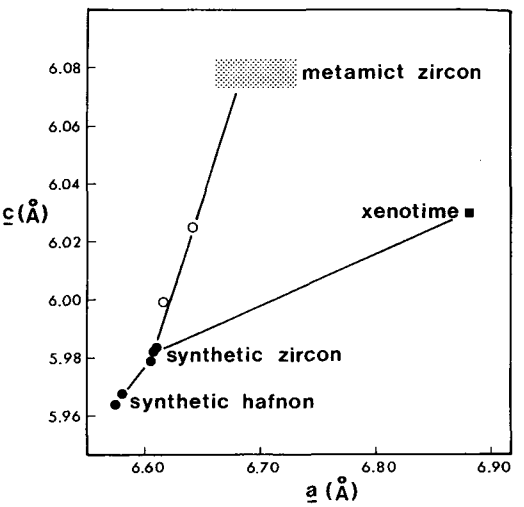

FIG. 6. Lattice parameters for synthetic zircon and hafnon, metamict zircon, isostructural xenotime, and coexisting domains in single crystals (open circles) (from Köppel and Grünenfelder, 1971).

radioactive decay of associated U. This would be most severe in the trace-element-rich domains where U exceeds 1%, resulting in an apparent correlation of trace-element concentration and lattice parameter.

The Lewisian zircons investigated in this study, however, have exceedingly low U concentrations, below the detection limit of the electron microprobe ($\sim$ 100 ppm). Therefore, no significant variation in the lattice parameters can be attributed to radiation damage. The concentration of (Hf + Y) is at maximum 2–3%. At this level, substitution of Hf reduces the lattice parameters by an insignificant amount along a line joining hafnon and zircon (fig. 6). Substitution of Y increases the lattice parameters along the line joining zircon and xenotime. The net change in a/c will be less than 0.15%.

In Laue photographs taken with the c-axis vertical and the incident X-ray beam normal to (100) or (110), spots of the type (hk0) form small clusters and exhibit both horizontal and vertical splitting with a maximum variation of θ of 0.5°. Since zircon is tetragonal with $a = b$, such splitting can only arise from slight misorientation of parts of the crystal.

In photographs with the c-axis horizontal and the beam incident normal to (010), (0kl) spots will be displaced by a variation in a/c, but only in the horizontal direction. The maximum expected variation in a/c due to Hf and Y substitution in these zircons would result in a change in θ(011) of only 0.02°, whereas in Laue photographs taken in this orientation, (0kl) spots are clearly multiple with splitting of the order of 0.5° both horizontally and vertically. The horizontal splitting thus far exceeds that due to variation in a/c and can be most plausibly attributed to misorientation.

We conclude, therefore, that although small changes in lattice parameter cannot be eliminated, the dominant cause of the observed splitting is the slight misorientation of parts of the crystal, probably associated with the sectors. Each multiple spot is composed of up to five individuals, suggesting that similar sectors are not identically oriented.

Acknowledgements. We are grateful to Drs P. Gay and M. G. Bown for advice on the interpretation of X-ray photographs and Dr R. W. Hinton for valuable advice and comment: also to Mr M. Haslop for mineral separations and K. Rickson for taking X-ray photographs. J.F.H. acknowledges the award of a Research Studentship by the NERC.

REFERENCES

Chase, A. B., and Osmer, J. A. (1966) *J. Electrochem. Soc.* **113,** 198–9.

Köppel, V., and Grünenfelder, M. (1971) *Schweiz. Mineral. Petrogr. Mitt.* **51,** 385–409.

—— and Sommerauer, J. (1974) *Contrib. Mineral. Petrol.* **43,** 71–82.

Krogh, T. E. (1982) *Geochim. Cosmochim. Acta,* **46,** 637–49.

Oberli, F., Sommerauer, J., and Steiger, R. H. (1981) *Schweiz. Mineral. Petrogr. Mitt.* **61,** 323–48.

Romans, P. A., Brown, L. L., and White, J. C. (1975) *Am. Mineral.* **60,** 475–80.

Sahama, T. G. (1981) *Bull. Mineral.* **104,** 89–94.

Speer, J. A. (1980) In *Orthosilicates* (Ribbe, P. H., ed.) Mineral. Soc. Am. *Reviews in Mineralogy,* **5,** 67–112.

[*Manuscript received 15 March 1983; revised 7 March 1984*]