

# Alteration of zircons: the evidence of Zr mobility during bauxitic weathering

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Zirconium is generally considered to be a relatively immobile element during weathering due to its chemical properties and high resistance of its most common mineral zircon. However, some mobility of Zr is proposed for different bauxite occurrences based on statistical calculations (Mordberg and Nesterova, 1996) and mineralogical observations (Melfi *et al.*, 1996). To extend the notion on Zr behaviour under the conditions of deep weathering, the alteration of zircons have been examined using as an example a Devonian bauxite deposit occurring within the Timan Folded Area, Russia.

The bauxite profile studied is developed over Pre-Cambrian carbonate strata altered by a metasomatic process producing an alkali association (K-feldspars,

albite, riebeckite and aegerine). The accessory minerals of the parent rock are pyrite, apatite, pyrochlore, columbite, monazite, zircon and ilmenite. Intercalated carbonate- and silicate-rich layers ranging in thickness from 0.5 to 5 cm form banded structures typical for this rock. A series of zones, from the bottom to the top of the profile have been recognised (Mordberg, 1997). At the base is a zone of carbonate leaching consisting mainly of strongly corroded feldspars with variable amounts of Fe oxides and hydroxides with remnants of calcite and dolomite, and an illite-hematite-kaolinite zone covering either the underlying rock, or the zone of carbonate leaching. Above is a zone of bauxitic clay consisting mainly of kaolinite and hematite, the latter often forms as a pseudomorph after pyrite. The bauxite zone is characterised by the predominance of boehmite; gibbsite and diasporite are present in amounts of less than 5%. Kaolinite and hematite also typically occur within this zone. Finally, a zone of redeposited bauxite, 0.5 to 4 meters thick, is characterised by a detrital texture and partial kaolinization. The profile attains a total depth of 100-120m and has a complex zonation resulting from selective weathering and substratum heterogeneity.

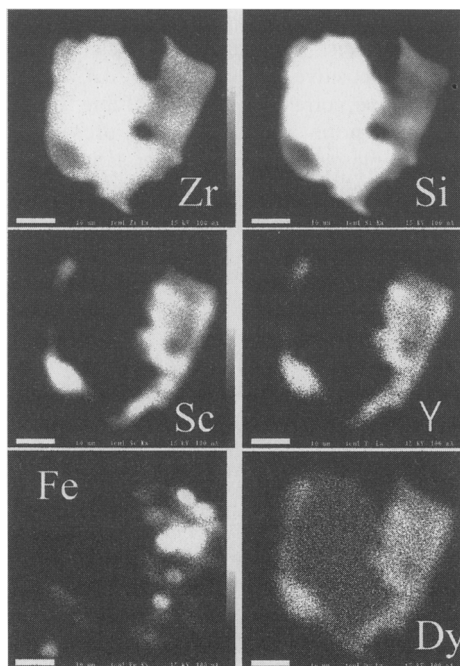


FIG. 1. The distribution of Zr, Si, Sc, Y, Fe and Dy within a zircon crystal. Scale bar = 10  $\mu\text{m}$ .

## Methods

Zircon was analysed using a wavelength-dispersive (WD) electron probe microanalyser (Cameca SX50) at the NHM, London. The analytical conditions used were 15kV and 20nA with counting times of 20s for: Zr, Ca, Ti, Nb, P, Sc, Pb, Mn, Fe, Hf, Na, Mg, Al, and Si, 30s for: La, Ce, Th, U, Pb, W, and 50s for Y, Pr, Nd, Sm, and Dy. Zr, Si and Hf were calibrated using zircon as standard (USNM 117288-3 SiO<sub>2</sub> 32.40% ZrO<sub>2</sub> 66.32% HfO<sub>2</sub> 1.06%). For the REE and Y, Ca, Si, Al and REE glasses were used, and Sc was calibrated using a synthetic ScPO<sub>4</sub> (USNM 168495, Jarosewich, 1991). Background positions used for the REE were those given by Williams, (1996). Elemental X-ray maps were obtained using the following conditions: 15kV 100nA 200 $\mu\text{s}$  per point.

TABLE 1. Chemical composition of 'pure' (18 analyses) and altered (15 analyses) zircons from 6 crystals (wt.%)

'pure' zircons					'altered zircons'				
	Mean	S.D.	Min	Max		Mean	S.D.	Min	Max
Na <sub>2</sub> O	0.01	0.01	0	0.03	Na <sub>2</sub> O	0.05	0.03	0.02	0.16
Al <sub>2</sub> O <sub>3</sub>	0.07	0.03	0.03	0.16	Al <sub>2</sub> O <sub>3</sub>	0.97	0.20	0.50	1.32
SiO <sub>2</sub>	31.6	0.31	30.7	32.0	SiO <sub>2</sub>	24.4	1.56	21.9	28.2
ZrO <sub>2</sub>	66.3	0.8	64.6	67.3	ZrO <sub>2</sub>	55.0	2.69	50.9	60.5
P <sub>2</sub> O <sub>5</sub>	0.11	0.06	0.01	0.27	P <sub>2</sub> O <sub>5</sub>	1.63	0.88	0.87	3.75
CaO	0.03	0.02	0	0.09	CaO	1.13	0.26	0.54	1.45
Sc <sub>2</sub> O <sub>3</sub>	0.04	0.02	0	0.09	Sc <sub>2</sub> O <sub>3</sub>	2.39	0.58	1.52	3.43
Y <sub>2</sub> O <sub>3</sub>	0.17	0.13	0.01	0.43	Y <sub>2</sub> O <sub>3</sub>	3.19	0.99	1.84	5.77
HfO <sub>2</sub>	1.45	0.41	0.86	2.34	HfO <sub>2</sub>	1.29	0.24	0.68	1.71
Total	99.9	0.95	96.8	101	Total	90.1	2.5	84.9	95.8
Y <sub>2</sub> O <sub>3</sub> /P <sub>2</sub> O <sub>5</sub>	1.52	1.00	0.26	4.44	Y <sub>2</sub> O <sub>3</sub> /P <sub>2</sub> O <sub>5</sub>	2.16	0.59	1.32	3.46

## Results and discussion

Anhedral zircon crystals, typically 5–40 µm in size, are dispersed in bauxite together with the other accessory minerals. The element distribution maps of one of the crystals (Fig. 1) show clearly that the core is composed of almost pure zircon, whereas the rim, presumably altered zircon, accumulates elements such as Y, Sc, Dy and Fe, in a rather heterogeneous manner. Microprobe analyses of these areas (Table 1) shows a very strong enrichment in the altered area by not only Y, P and Sc, but also Na, Ca and Al. The contents of Al and Ca are within ranges reported for zircon; however, the content of Sc<sub>2</sub>O<sub>3</sub> (up to 3.43 wt.%) is higher than it is known for zircons. Hf is the only element which occurs in 'altered' zircon in slightly lower amounts.

The composition of 'pure' zircon corresponds closely to ideal stoichiometry, whereas the composition of altered zircon deviates from this ideal because of a depletion of SiO<sub>4</sub>. The low analytical total suggests that the altered zircon is metamict, and evidence the presence of essential H<sub>2</sub>O (as well as adsorbed H<sub>2</sub>O in radiation-induced defects in metamict zircons (Speer, 1982). The analysis of correlation matrices of element contents in zircon (Table 2) shows several features. In both 'pure' and altered zircons, there is a high positive correlation of Y and P that points to the presence of xenotime in solid solution with zircon. In altered zircon, the correlation of Y and P is even higher and the presence of sufficient xenotime admixture does not rise doubts. In the altered zircons, Sc does not correlate with Y or P but correlates positively with Al and Ca. The observed ratio Y<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub> in altered

zircons (Table 1) is higher than the calculated value in xenotime (1.59), therefore, the presence of ScPO<sub>4</sub> is unlikely, though some substitution of Sc for Y is possible. A very high positive correlation of Ca with Al together with their high contents suggests that these elements occur in separate mineral phase. Assuming all silica is combined with Zr, we calculate the amount of "redundant" ZrO<sub>2</sub> using the formula

$$\text{ZrO}_{2(\text{redundant})} = \text{ZrO}_{2(\text{total})} - 2.05 \times \text{SiO}_2;$$

It is of interest, that calculated redundant ZrO<sub>2</sub> shows a high positive correlation with Al, Ca and Sc, and a negative correlation with Si (Table 2). Such correlations point clearly to the presence of submicroscopic inclusions of another as yet unidentified mineral phase, which is dominantly composed of Ca, Al, Sc and Zr.

The 'pure' zircon crystals within the bauxite profile may considered to have been inherited from the parent rock. Of the Zr within the bauxite, a proportion will be incorporated within this zircon, and therefore be relatively immobile. However, Zr present in the primary rock-forming minerals e.g. riebeckite and aegirine will have been released and attained some degree of mobility within the altered profile, subsequently forming secondary minerals, rich in Ca and Al, as altered rims to the 'pure' zircon. The geochemical role of Sc is unclear within the weathering environment, but apparently follows Ca and Al rather than Y, and forming discrete, as yet unidentified, secondary minerals associated with the altered zircon. The observed Zr-rich alteration zones around primary zircon crystals demonstrate this element to have undergone some degree of mobility and redistribution during deep bauxitic weathering. This mobility is however, restricted to the weathered profile.