EXPERIMENTAL INVESTIGATION OF THE ASSOCIATION ZIRCON-MANGANOTANTALITE IN HIGHLY-FLUXED PEGMATITIC SYSTEMS

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INTRODUCTION

In the Tanco pegmatite, zircon is intimately associated with Ta mineralization, and considerable amounts of Ta can be incorporated in the zircon (Van Lichtervelde et al. 2009). This association has been investigated experimentally through 1) dissolution experiments of zircon and manganotantalite in highly-fluxed pegmatitic melts, which reveals a competition of Zr and Ta for the structural sites in the melt; 2) crystallization of Ta-doped zircon from a Li-Mo flux in order to determine the substitution mechanisms leading to Ta incorporation in zircon; and 3) crystallization experiments of associated zircon and manganotantalite from pegmatitic melts, in view to determine the temperature-dependence of Ta-in-zircon and Zr-in-tantalite incorporation.

DISSOLUTION EXPERIMENTS OF ZIRCON AND MANGANOTANTALITE

Dissolution experiments of pure synthetic zircon and manganotantalite, either coexisting or not, were conducted at 700 to 1000ºC and 200 MPa in highly-fluxed, water-saturated pegmatitic melts. The investigated melts are synthetic but their compositions were chosen to match as close as possible the conditions in natural pegmatites, in particular the compositions of the different ore-bearing zones in the Tanco pegmatite. The ASI (aluminium over alkali atomic ratio) ranges from peralkaline to peraluminous (ASI_{Li} = Al/[Na+K+Li] = 0.76 to 1.28) with various K/Na ratios, and the melts were enriched in flux elements: 1-1.7 wt% Li_2O, 2-5.5 wt% F, 2-4 wt% P_2O_5 and 0-2.8 wt% B_2O_3. Pure synthetic, end-member manganotantalite and zircon were used in order to avoid problems with slow solid-state kinetics, but additional experiments using natural manganotantalite and zircon of relatively pure composition (i.e., close to end member composition) displayed similar results. Zircon and manganotantalite solubilities considerably increase from peraluminous to peralkaline compositions, and are more sensitive to changes in temperature or ASI of the melt than to flux content. The solubility data reveal a small but significant competitivity of Zr with Ta for the structural sites of the melts (Fig. 1). This competitivity increases from peraluminous to peralkaline compositions, and suggests an affinity of Ta for Al complexes whereas Zr is more easily complexed by alkali.

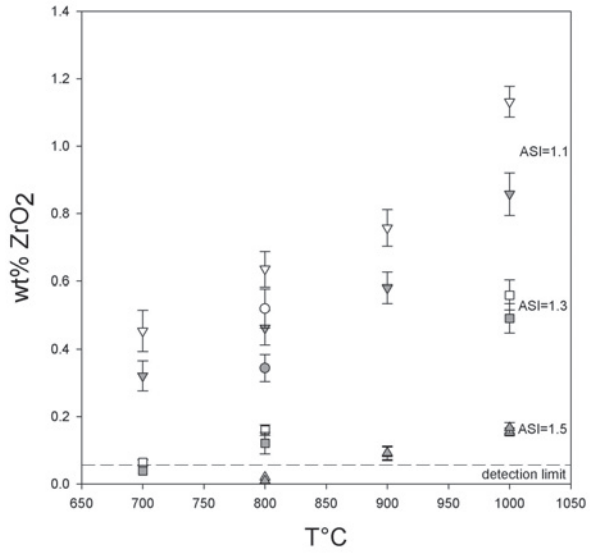

Figure 1- Solubility of zircon (1σ errors) in melts of different ASI. White symbols are dissolution experiments of zircon only, whereas gray symbols are dissolution experiments of zircon + manganotantalite.

CRYSTALLIZATION OF TA-DOPED ZIRCON FROM LI-MO FLUX

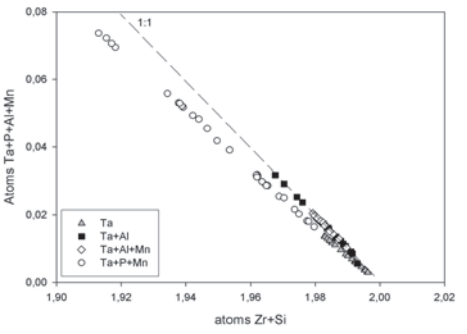

Figure 2 - Trends in synthetic zircons doped with Ta and other elements

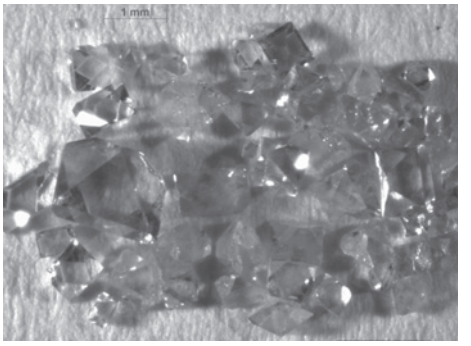

Figure 3 - Synthetic zircon crystals

Zircon crystals up to 5 mm in size (Fig. 2) were synthesized from a Li-Mo flux following the method of Hanchar et al. (2001). With this method, the Li-Mo flux is doped with stoichiometric amounts of Zr and Si, placed in a ventilated furnace at 1 atm and slowly cooled down with a rate of 4ºC/h during 2 to 3 days. The batches were doped with various amounts of Ta, Al, P and/or Mn. The results show that considerable amounts of Ta can be incorporated in zircon even in the absence of

other doping elements, and it is suspected that Li plays a significant role in charge-balancing the reaction: $Ta^{5+} + 3Li^{+} = 2 (Si^{4+}, Zr^{4+})$. In the presence of P^{5+}, much smaller amounts of Ta are incorporated into zircon, suggesting that P^{5+} competes with Ta^{5+} in tetrahedral sites. Manganese is incorporated only in the presence of P and has no interaction with Ta. In the presence of Al^{3+}, the stoichiometric reaction $Al^{3+} + Ta^{5+} = 2 (Si^{4+}, Zr^{4+})$ occurs. However, if Al^{3+} is absent of the reaction, the number of Ta±P±Mn atoms does not equal the missing number of Zr+Si atoms (Fig. 3), which strongly suggests the presence of Li (not yet analyzed) in the reaction.

CRYSTALLIZATION EXPERIMENTS OF ASSOCIATED ZIRCON AND MANGANOTANTALITE FROM PEGMATITIC MELTS

Crystallization experiments from the same pegmatitic melts as for dissolution experiments were conducted to determine the composition of coexisting zircon and manganotantalite. The glasses were doped with Zr and stoichiometric amounts of Mn+Ta. The experiments were conducted between 900 and 1200ºC at 200 MPa in internally-heated Ar-pressure vessels equipped with rapid quench systems. The grown crystals were up to 50 µm in size. Several types of experiments were conducted (Fig. 4):

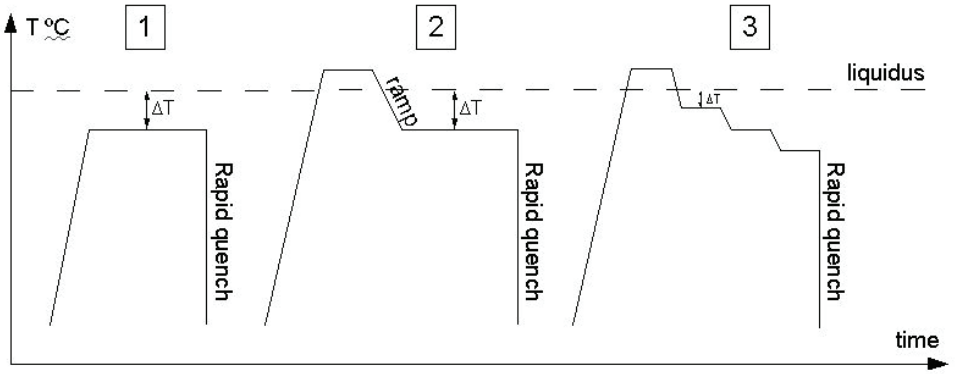

Figure 4- different types of crystallization experiments

The runs are heated up directly to a temperature below the zircon and manganotantalite liquidus. Independently on the ΔT, the runs display very fine-grained (<2µm) crystals of zircon and manganotantalite with high density of nuclei. Both the glasses and the crystals cannot be analyzed reliably.

The runs are in a first step conducted at 1250ºC (above the liquidus) for 24h, then cooled below the liquidus temperature with different cooling rates and degrees of undercooling (ΔT), and left at the final temperature (900 to 1150ºC) for another 3 to 5 days.

In order to avoid strong undercooling, the runs were cooled progressively with small ΔT steps everyday, resulting in zoned crystals. The rims of the crystals are thought to correspond to the last temperature of the experiment and equilibrium crystallization is guarantied.

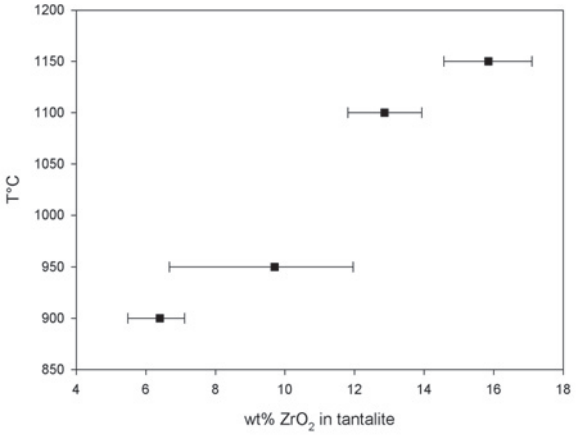

Figure 5- Temperature dependence of Zr-in-tantalite

In all experimental runs, manganotantalite and zircon displayed high concentrations of Zr and Ta, respectively (up to 20 wt% ZrO_2 in manganotantalite and 2 wt% Ta_2O_5 in zircon). In manganotantalite in equilibrium with zircon, ZrO_2 concentrations are dependent on temperature (Fig. 5). In the second type of experiments, high degrees of undercooling (more than 200ºC) lead to the formation of dendrites of manganotantalite such as those which can be observed in the external zones of the Tanco pegmatite (Fig. 6), where the magma was supercooled in the vicinity of country rock xenoliths. Such crystals display particularly high crystal-to-melt Zr partition coefficients which reflect disequilibrium, and zircon does not even nucleate in those experiments.

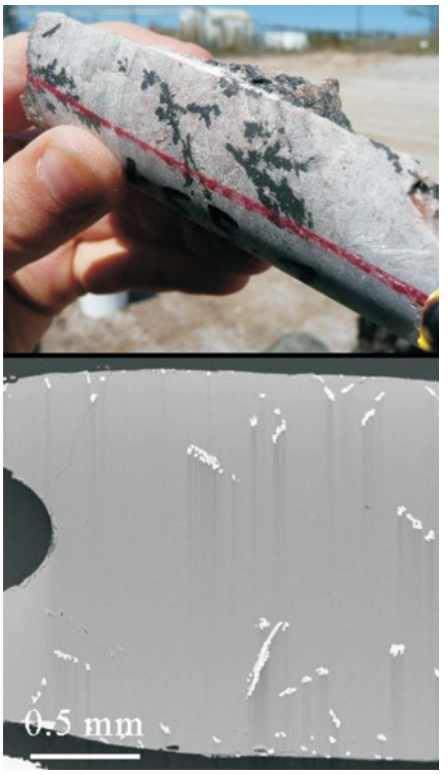

Figure 6- Dendrites of manganotantalite in the Tanco pegmatite (up) and in an experiment at 1000ºC (down) supercooled by 250ºC in 3 min.

CONCLUSION

The experimental data with manganotantalite and zircon associated together is useful to understand the association of these two minerals in rare-element granites and pegmatites, in particular the affinity of Zr for peralkaline systems whereas Ta can be concentrated in peraluminous systems. The example of the different Tanco zones will be discussed. In natural samples in which zircon and manganotantalite crystallized together, the Zr contents in tantalite could be used to estimate the temperature of crystallization.

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