Tectonic activity recorded by multiple episodes of zircon growth: an ion microprobe (SHRIMP) study of the geological evolution of the Cyclades, Greece

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To interpret the significance of multiple episodes of zircon growth, the processes controlling zircon growth must be distinguished. There is currently little agreement concerning the origin and significance of metamorphic zircon and how it can be related to pressure-temperature-time (P−T−t) paths (cf. Fraser *et al.*, 1997; Roberts and Finger, 1997). New zircon growth has been attributed to a number of different processes: (1) melt crystallisation; (2) net-transfer reactions; (3) hydrothermal precipitation; or (4) solid-state recrystallisation/replacement processes. Each of these mechanisms has different implications for the interpretation of zircon ages. As zircon remains closed to isotopic exchange at temperatures in excess of those commonly experienced during either metamorphism or magmatism, zircon ages will generally record the time of growth rather than the time of cooling below its closure temperature. While dating of different layers of zircon can constrain the time of zircon growth it will not shed light on the zircon formation mechanism. To help interpret zircon ages in terms of tectonic processes it is necessary to study zircon morphology, internal structure and chemistry and to try and relate this to the textural relations and chemistry of the zircon host rock.

Regional setting. The tectonic evolution of the Cyclades during the Alpine orogeny includes polyphase metamorphism, deformation, fluid infiltration, anatexis and shearing. Hence the Cyclades provides a natural laboratory to assess the behaviour of zircon developed in response to different mechanisms. The Cyclades consist of a Hercynian orthogneiss basement, in unconformable contact with a variegated series of Mesozoic marbles, schists and metavolcanics (Dürr *et al.*, 1978). During the Alpine orogeny these rocks experienced an Eocene high pressure metamorphism (M_1) overprinted by Oligo-Miocene greenschist-amphibolite facies medium pressure metamorphism (M_2). They form the lower plate to a sequence of metamorphic core complexes exposed in the Aegean (Lister *et al.*, 1984). The upper plate is comprised of ophiolites, Upper Cretaceous/Permo-Triassic limestones and granitoids that have experienced Cretaceous high temperature, low pressure metamorphism but have not experienced any Alpine metamorphism (Reinecke *et al.*, 1982), along with unmetamorphosed sediments and volcanics.

Methods. Zircons were separated from rock units that had experienced Alpine orogenesis from the islands of Naxos, Ios and Sifnos. They were imaged using cathodoluminescence techniques to identify internal zircon structures and choose potential target sites for analysis. Layers that could clearly be identified as new growth, potentially related to metamorphism, were preferentially analysed. U, Th and Pb/U in the sample zircons relative to those in the SL13 reference zircon were measured using the sensitive high resolution ion microprobe (SHRIMP). The main advantage in using SHRIMP for U-Pb dating, as opposed to conventional isotope dilution techniques, is that it allows the analysis of = 30 μm areas within mineral grains and thus the measurement of ages for different growth zones. To ensure no 'mixed ages' occurred due to spatial overlap of more than one growth zone by the probe, all mounts were imaged after analysis to check the actual pit location. Assessment of the age data-sets for the presence of discrete age populations was carried out both by construction of age probability distributions and by a mixture-modelling procedure.

Zircon characteristics. The identification of multiple layers of metamorphic zircon growth is made according to zircon morphology, internal structure and chemistry. In general, magmatic zircon growth is characterised by the development of oscillatory zoning while metamorphic zircon is generally unzoned, displays low luminescence and has variable, but generally low Th/U ratios. However, zircons produced by small degrees of partial melting can appear as unzoned, low luminescent overgrowths preferentially nucleated on grain terminations (Keay *et al.*, 1998). Partial melting at high metamorphic grade can produce zircon of this form, however, the majority of Cycladic rocks have not experienced temperatures in excess of ~ 600°C, and so the formation of new zircon must be related to sub-solidus processes. Zircon formed by such processes occurs as distinct overgrowths, clearly truncating earlier growth structures, is distinctly younger than the protolith age of the host rock and occurs in metasediments that have not experienced partial melting. As there is no textural evidence to suggest the operation of in situ net-transfer reactions, and the zircon morphologies are not consistent with recrystallisation, the most likely origin of such overgrowths is by hydrothermal precipitation.

Evidence for zircon growth related to fluid infiltration. Numerous stable isotope studies of the Cyclades have shown that limited permeability and structurally-controlled fluid infiltration has occurred associated with the M_2 metamorphic overprint. Fluid influx before and during M_1 is likely to have occurred in response to mineral breakdown reactions and during sea-floor alteration of the protoliths prior to metamorphism. Samples that contain new zircon growth have stable isotopic signatures characteristic of fluid infiltration, consistent with the hypothesis that the new zircon was hydrothermally precipitated. It is significant that the development of new zircon growth in sedimentary rocks that have not undergone anatexis is mainly restricted to calc-silicates. This suggests that the calc-silicates behaved as permeable media, a suggestion supported by stable isotope evidence, but this could also relate to the intrinsic chemical properties of the calc-silicates. Mobility of zirconium in fluids is enhanced if the Zr can be transported as a fluoride complex. As such solutions are mildly acidic they may precipitate zirconium when transported into a reactive medium like the relatively alkaline calc-silicates.

Zircon age populations. Zircon ages cover the entire Alpine evolution of the Cyclades from the Cretaceous to the middle Miocene. As zircon development occurs in response to external factors that are likely to broadly correlate with tectonic events, combining these ages allows some broad generalisations to be made about the relationship between the formation of metamorphic zircon overgrowths and tectonic events in the Cyclades. Clusters of ages in the ranges 140–120, 105–95, 80–70, 50–40, 35–30, 18–17 and 14–13 Ma can be identified, suggesting that these were periods of active tectonism. These periods of new zircon development are difficult to relate to P–T conditions as they occur in response to processes that have affected the host rock that are no longer visible in the main mineral assemblage due to overprinting by younger events. It is unclear what sort of tectonic process may have led to the development of new zircon growth in the two oldest age ranges, but the strong cluster of ages at 80–70 Ma corresponds to the timing of ophiolite formation on Syros and also the timing of high-T metamorphism in the Cycladic Upper Unit.

Ophiolite formation in the Cyclades was accompanied by sea-floor alteration prior to early Tertiary subduction/collision, producing a crustal sequence containing large quantities of water in the form of chlorite and clay minerals that would devolatilise during high-P metamorphism. The significant period of zircon growth between 50–40 Ma is interpreted as recording fluid infiltration during the transition from eclogite to blueschist facies metamorphism post-peak M_1 and is consistent with estimates of the timing of M_1 from other isotopic systems. Retrogression to greenschist facies conditions and further fluid influx is recorded by zircon ages of 35–30 Ma. This was followed by localised migmatisation and the development of new zircon during the late stages of partial melting (Roberts and Finger, 1997) at 18–17 Ma associated with M_2. Crystallisation of these partial melts led to post-peak M_2 release of water to form the youngest layers of zircon growth at 14–13 Ma. These youngest zircon ages correlate with SHRIMP U-Pb ages obtained from monazite and titanite from related Cycladic samples, all of which are interpreted to have formed in response to shearing related to extension during post-peak M_2 metamorphism.

Summary. Multiple metamorphic episodes related to *fluid infiltration* have been identified in the Cyclades from SHRIMP U-Pb dating of zircon overgrowths. The reproducibility of ages from different samples from different areas of the Cyclades and their consistency with other geological evidence suggests that zircon can be used to constrain the tectonic history of complicated orogenic belts. As most of the Cycladic rocks have not experienced temperatures in excess of ~600°C, the formation of new zircon must be related to sub-solidus processes, such as fluid infiltration. Stable isotope evidence suggests that zircon growth in Cycladic rocks can be related to hydrothermal activity and this is facilitated by the geochemical nature and the degree of deformation of the host lithology. As the fluid infiltration history of the Cyclades can be reasonably well-constrained, it is possible to use the time of hydrothermal precipitation of zircon in the construction of P–T–t paths for the area.