

Shallow crystallization and deep magma storage: Insights from U-Th and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

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Precise $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations and ^{238}U - ^{230}Th analyses from volcanoes atop vastly different thicknesses of crust in four subduction zones reveal new insights about the temporal and physical development of arc magmatic systems over several tens of thousands of years. Analytical advances yield $^{40}\text{Ar}/^{39}\text{Ar}$ ages and U-Th mineral isochrons for latest Pleistocene to Holocene lavas and tephra with uncertainties of only a few thousand years. Thus, quantifying the length of time between crystallization and eruption has become more robust and crystallization-eruption intervals may be calculated over the lifetime of an individual volcano; this represents a significant advance in linking volcanic evolution to magmatic processes as compared to restricting U-Th geochronology to historical eruptions. Our most compelling discovery is that minerals (opx, cpx, mt, plag, ol), matrix glass, and whole rocks measured in dozens of basaltic to rhyolitic lava flows and pyroclastic deposits erupted over the last ~150 ka define ^{238}U - ^{230}Th isochrons whose age cannot be distinguished from that of the eruption. This finding indicates that the observed phenocrysts began to grow less than 1 to 2 ka prior to eruption and that processes including crystal fractionation and magma mixing—required to explain the spectrum of basaltic to rhyolitic compositions erupted at these volcanoes—took place *prior* to growth of the erupted crystals. The short crystal residence times are consistent with inferences from trace-element zoning and diffusion profiles in phenocrysts and ^{226}Ra - ^{230}Th disequilibrium data from recent eruptions at several volcanoes, each of which likely reflect exceptionally rapid transit of evolved melt through the crust, during which crystallization of the erupted phenocrysts occurs *en route* due to decompression.

The duration of magma storage and processing in the deep crust, although more difficult to constrain, can be tracked using initial ($^{230}\text{Th}/^{232}\text{Th}$) ratios in sequences of lavas and tephra erupted over 10^4 - 10^5 year periods of volcano growth that have been precisely dated using $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. Our large set of ^{238}U - ^{230}Th data suggests that the duration of deep crustal storage, differentiation and mixing of magma may vary greatly, ranging from a few thousand years to longer than 100 ka. In most cases, it appears that the deep crust buffers mafic magma flux from the mantle, which may explain our finding that long-term arc volcano growth rates are modulated to within a narrow range, despite gross differences in crustal thickness or age.

Oxygen isotope record of Devonian and Carboniferous biogenic apatite

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Oxygen isotopes of conodont apatite (n=1286) were studied in order to reconstruct the palaeotemperature and ice volume history during the Devonian and Carboniferous. Oxygen isotope ratios are around 18‰ V-SMOW in the Early Devonian, increase gradually during the Pragian and Emsian, show comparatively high values around 20‰ V-SMOW in the Middle Devonian, decrease during the early Frasnian to minimum values around 18‰ V-SMOW at the Frasnian-Famennian transition, and increase again to 19‰ V-SMOW in the Famennian. The Early Carboniferous record is characterized by a first major increase to values around 21‰ V-SMOW in the middle Tournaisian to earliest Viséan, high values around 21‰ V-SMOW in the Viséan and a second major increase in the Serpukhovian to maximum values around 23‰ V-SMOW. Oxygen isotope values of Pennsylvanian and Early Permian conodont apatite vary between 19 and 22‰ V-SMOW.

The $\delta^{18}\text{O}$ fluctuations recorded in the Devonian are interpreted as palaeotemperature changes with the Early and Late Devonian revealing relatively warm climatic conditions, whereas the Middle Devonian is characterized by a cooler climate. The positive shifts in the oxygen isotope ratios in the Tournaisian and Serpukhovian are too large to be explained solely by a change in sea water temperature and/or salinity. Instead, the 2‰ positive shift in the Tournaisian argues for a first major cooling and glaciation event in the Tournaisian with ice masses persisting into the Viséan. The 1.5‰ shift in the Serpukhovian points to an intensified ice build-up during the latest Mississippian. The relatively large variance in the oxygen isotope ratios of Pennsylvanian conodonts is explained by the waxing and waning of Gondwanan ice sheets.

The comparison of the conodont apatite with published brachiopod calcite $\delta^{18}\text{O}$ records (taking into account the different thermodynamic oxygen isotope fractionations for apatite and calcite) reveals that $\delta^{18}\text{O}$ values of apatite are in many cases significantly higher than calcite $\delta^{18}\text{O}$ values. Apatite $\delta^{18}\text{O}$ values translate into realistic palaeotemperatures by assuming a modern $\delta^{18}\text{O}$ value for Palaeozoic sea water and do not support the idea of a secular change of the oxygen isotope composition of sea water.