

Where is geochronology going? Alteration and mineral mixtures

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Ore geologists owe their living to water released by crystallizing granitoids. This fluid phase shows enhanced activities of aggressive anions, and wall rocks. Do contact aureoles teach us universally applicable principles?

"Alteration" of a mineral is its modification by a different process from its formation. Metamorphic processes are a subfamily of alteration; the connection becomes even more obvious if one considers that the modern consensus on metamorphism stresses the great importance of fluids.

The perception of "minerals" has been greatly modified by electron beam analyses. TEM and EMP have shown a whole new world in which minerals are no longer as simple as was believed 50 years ago: inclusions, inter/overgrowths, replacements and relics are now considered to be ubiquitous. How can geochronologists adapt to a changing paradigm, according to which most carrier phases of the isotopes used for dating are mixtures?

Real progress in zircon dating was achieved when cathodoluminescence images were coupled to sensitive spot analyses. Petrographic and textural criteria were used to guide the interpretation of isotope analyses. Accretion of hydrothermal or metamorphic rims was shown to be one of the principal mechanisms causing discordance. This ended a 40-year-old dispute on the role of diffusive losses: it is now certain that diffusion is a very slow process which always will be overrun by recrystallization whenever water is available.

After the door was opened, other minerals also benefitted from detailed petrographic characterizations. A common pattern emerged: monazite can record younger ages at the core of a crystal than at the rim - matching with recrystallization textures; muscovites give different laser Ar-Ar ages as a function of shear-induced recrystallization or of their Si content, a monitor of their differential recrystallization under changing PTAX conditions.

Accepting the petrographic evidence that many minerals are polygenic mixtures rather than homogeneous gems must open up new paradigms for isotope geologists. If each mineral generation can retain the elemental and isotopic record of its formation, it becomes necessary to discriminate the signature of each. When laser ICP or laser Ar-Ar analyses are not sufficiently precise, it is possible to exploit an alternative technique. Stepwise release experiments contain chemical information, e.g. the Th/U and Pb/U, or Ca/K and Cl/K element ratios given by Pb and Ar isotopes, respectively. This must be tied to electron microprobe analyses so as to firmly identify the isotope reservoirs and assign each of them an individual age.

Example: Pb/Pb and Cl/Ar ratios in contact halo K-fsp (Sardinia) correlate with deuteric replacement textures.

Re-calibration of surface complexation models for magnesite and dolomite using Brown valence theory and a genetic algorithm

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The CD-MUSIC (Charge Distribution MULTIsite Complexation) model offers a novel theoretical framework to study surface complexation on oxide minerals [1]. The model reconciles the bulk mineral crystallography with chemical and thermodynamic notions traditionally invoked by earlier models.

The first step in exploring the relevance of multi-site complexation to carbonate minerals is to estimate a new set of surface parameters derived from crystal chemistry and Brown-valence theory in order to re-calibrate existing models of surface complexation.

We estimated the density and residual charges of different reactive surface sites on the (104) plane of magnesite and dolomite according to the protocol applied to oxides [2]. These parameters were used to reformulate an earlier conceptual model of surface complexation for magnesite and dolomite in which integer rather than fractional residual charges were assigned to the surface sites [3,4].

Re-calibration of the surface complexation models was carried out by fitting values of the intrinsic complexation constants using published data of surface charge [3,4]. To this end, an in-house computer code was used. The code incorporates a genetic algorithm as a novel stochastic search and optimization technique. The intrinsic constants we obtain are similar to those reported in previous studies [3,4] and allow the simulation of the electrokinetic properties of both minerals under varying conditions of pH, ΣCO_2 and total metal concentration

The implications of our results for modeling multi-site complexation at the mineral-water interface of Ca-Mg rhombohedral carbonates will be discussed.

References

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