

## Zr-in-Rutile and Ti-in-Quartz Thermometry Support a Metasomatic Origin for the Pea Ridge Iron Oxide-Apatite-REE Deposit, Southeast Missouri, USA

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The role of Fe-rich melts and Fe-metasomatism in the generation of iron oxide-apatite-REE deposits remains controversial. Trace element thermometry provides a robust method of constraining the temperatures of mineral growth or recrystallization associated with igneous and hydrothermal events, especially in cases where mineral assemblages are not amenable to traditional thermometry. The southeast-dipping dike shaped Pea Ridge iron oxide-apatite-REE deposit is hosted dominantly in subalkaline porphyritic rhyolitic with minor trachytic volcanic rocks. The central magnetite ore zone is capped by hematite, with an amphibole-quartz zone in the hanging wall and a K-feldspar-quartz dominant silicified zone in both the hanging- and footwall. Late-stage REE-rich breccia pipes cut the iron ore and silicified zones. Temperature conditions in each zone and the REE-rich breccia pipes are poorly constrained.

Zr-in-rutile and Ti-in-quartz equilibration temperatures were calculated assuming unit activity and lithostatic  $P = 0.75$  kbar assuming ~3 km depth for the alteration zones and hydrostatic  $P = 0.25$  kbar for the breccia pipes. In the magnetite ore zone Zr-in-rutile temperatures on rutile in magnetite crystal cores are ~490° to 500°C, where as those in rims and adjacent matrix are ~500° to 540°C. Rutile from the surrounding silicified zone yield temperatures of ~660° to 680°C (cores) and ~610° to 640°C (rims) for concentrically zoned crystals with bright and dark back scatter electron image (BSE) domains, respectively. Rare rutile inclusions in magnetite grains from amphibole-quartz zones yield equilibrium temperatures of ~640° to 660°C and ~460° to 80°C for bright BSE oscillatory zoned rutile and dark BSE rutile, respectively. In the magnetite ore zone Ti-in-quartz thermometry on both bright cathodoluminescence (CL) quartz inclusions in associated magnetite and on matrix quartz yield temperatures of ~490° to 530°C, similar to Zr-in-rutile estimates. However, darker CL recrystallized quartz cores preserved in the matrix record lower temperatures of ~380° to 440°C. The silicified zone yielded Ti-in-quartz temperatures of ~570° to 610°C for bright CL oscillatory growth bands and temperatures of ~450° to 560°C for darker recrystallized domains. The amphibole-quartz zones preserve slightly cooler temperatures of ~570°C and ~460° to 480°C for bright and dark CL matrix quartz, respectively. Quartz phenocrysts in K-spar altered rhyolites peripheral to the deposit yield minimum temperatures of ~600° to 620°C and ~530° to 590°C for bright and dark CL oscillatory growth bands, respectively. Recrystallized dark CL matrix quartz in REE breccia pipes has Ti-in-quartz temperatures  $\leq 350^\circ\text{C}$ .

Most of the data suggest that the magnetite ore and surrounding silicified zones formed under relatively high temperature metasomatic conditions that cooled outward of the center of the deposit. Textural relationships suggest that some of the highest temperatures are on relict grains of igneous quartz and rutile that remained in the rock after metasomatic replacement by magnetite and silicate minerals. The late-stage REE-rich breccia pipes formed at much lower temperatures.