

1.4.P14**Zeolite solid solutions as buffers of the chemical potential of SiO₂**

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Rock-forming zeolites often exhibit complex solid solutions reflecting isomorphous substitutions between Si and Al in tetrahedral framework sites, between charge-balancing extraframework cations, and between water molecules and vacancies. Aside from zeolites in which coupled NaSi-CaAl substitution is observed (e.g., thomsonite and phillipsite), Si-Al substitution can be described by a hypothetical pure SiO₂ (+/- H₂O) endmember. This includes the common zeolites analcime [1] and stilbite [2] for which NaAl substitutes for Si, and chabazite and heulandite-clinoptilolite minerals for which Si-Al substitution appears to be independent of extraframework substitutions. In these cases, recent calorimetric, structural, and theoretical investigations suggest that Si-Al substitution can be described by non-ideal, athermal solid solution models characterised by no excess enthalpies of mixing and negative excess entropies of mixing [1,2,3,4]. Because Si-Al exchange in these minerals can be explicitly or implicitly described by exchange of an SiO_e component, the Si/Al ratio in their framework can be predicted solely as a function of temperature, pressure, and the chemical potential of SiO₂ (represented by the activity of aqueous silica). Application of this model leads to calculated Si/Al ratios in stilbite (coexisting with albite or analcime), analcime, chabazite, and heulandite-clinoptilolite consistent with observed mineral compositions and parageneses in very low-grade metamorphic environments and explains the absence silica polymorphs despite the fact that the aqueous phase associated with their formation is supersaturated with respect to quartz and other silica polymorphs.

References

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1.4.P15**The present state of the Fe-Co-Ni-As-S system**

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Combining the results of our investigations [1,2] of this system with literature data [3,4,5], yield a complete model of the phase-relations in the volume (Fe,Co,Ni)(As,S)₂.

At 650EC, the central portion of the prism, close to the (Fe,Co,Ni)AsS level, is dominated by the cobaltite-gersdorffite solid solution coexisting with arsenopyrite. There are three more sulfarsenides present: CoAs_{1.5}S_{0.5}, NiAs_{1.5}S_{0.5} and CoAs_{0.5}S_{1.5}, all displaying extensive substitutions. The former has an allosite type structure, while the two latter have pyrite type structures. Assemblages richer in S contain: mss + As-S melt, pyrite, vaesite and/or cattierite. The As-richest assemblages involve diarsenide solid solution, löllingite and krutovite as well as skutterudite and pyrrhotite.

At 500EC the phases in locate close to the MeAsS level are allosite, arsenopyrite, cobaltite and gersdorffite. These coexist with pyrite, cattierite or vaesite in S-rich assemblages and, löllingite, krutovite, safflorite, diarsenides solid solution as well as skutterudite and pyrrhotite in As-rich assemblages.

The most problematic region of this system is the NiS₂-NiAs₂ join, where the relative stability of phases is unclear. Especially interesting is the relation between the NiAs₂ polymorphs: rammelsbergite, pararammelsbergite and krutovite.

References

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