Experimental study of mineral equilibria in the system Li_2O-K_2O-Al_2O_3-SiO_2-HF-H_2O (with topaz) at 400°C and 100 MPa

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The experimental study of mineral equilibria in the system Li_2O-K_2O-Al_2O_3-SiO_2-HF-H_2O was carried out to determine influence of composition of solution (lithium content) on genesis of greisen deposits.

Topaz one of the major indicators of F-bearing minerals participating in most of the studied reactions. Experiments were performed in autoclaves in gold ampules with self-sealing shutter by a technique of monovariant reaction. This technique is based on change of topaz grain weight. All the mineral phases participating in the reaction were placed together into ampoules. The topaz was used as rounded grain whereas other components of reactions were added as powder. As a result influence of lithium on shift of topaz stability field on the diagram $\lg_{(mHF)} - \lg_{(mKF)}$ established earlier [1] for modeling system K_2O-Al_2O_3-SiO_2-HF-H_2O has been estimated. At low concentration of LiF and high concentration of HF in the solution the line limiting the topaz field for monovariant equilibrium topaz-AlF_3 moves downwards to the axis $\lg_{(mHF)}$. Muscovite stability field is replaced by lepidolite field at relatively high concentration of LiF and low concentration HF in the solution. Absence of potassium in the solution leads to formation of the lithium-bearing alumina-fluoride phase.

[1] Shapovalov Yu.B. (1988) *The collection of articles on physical & chemical petrology*, V.15. P.160-167 (in Russian)

Krypton and xenon in air bubbles from ice cores as tracers of past ocean temperature

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The heavy noble gases krypton and xenon are quite soluble in liquid water, with a strong temperature-dependence of the solubility. Because the total inventory of these gases in the ocean-atmosphere system is constant, an increase in the oceanic inventory must be accompanied by a complementary decrease in the atmospheric inventory. Dinitrogen (N_2) gas is much less soluble and so its atmospheric inventory is little affected by ocean temperature change. Sources and sinks of N_2 may be neglected due to the great abundance of this gas in the atmosphere, and the fact that the entire denitrifiable inventory of N comprises less than 0.01% of the atmospheric pool. Thus the ratios Kr/N_2 and Xe/N_2 in the past atmosphere should predominantly reflect past ocean temperature change. These parameters may be estimated from measurements of trapped air composition in ice cores, making appropriate corrections for gravitational settling and thermal fractionation that occurred in the snow layer (firn) at the ice core site. Measurements are done by classical dual- dynamic-inlet electron impact mass spectrometry on air melt-extracted from 1 kg of ice, and encompass the krypton isotope pair $^{86}Kr/^{82}Kr$ and $^{15}N^{14}N$ for the purpose of making the gravity and thermal corrections.

This new proxy reflects mean ocean temperature change, albeit slightly weighted toward the cold end of the temperature distribution due to the greater solubility of these gases in cold water. Because the ocean's heat and gas burdens are set at the outcrop where air-sea equilibration last occurs, and they travel through the ocean interior nearly adiabatically and conservatively, there is no time lag between changes in ocean heat content and changes in atmospheric noble gas burden. Consideration of the solubilities and relative volumes of the reservoirs leads to the prediction that a 1°C warming will produce a +0.5‰ increase in atmospheric Kr/N_2. Current measurement precision is around 0.2‰ for a 1-kg piece of ice, suggesting a precision of about 0.4°C for this proxy. Reconstructions over the past glacial cycle suggest a glacial mean ocean temperature about 3°C colder than present, with a rapid warming of about 2°C between 18-15 ka. This was a time period of rapid atmospheric CO_2 increase, consistent with the hypothesis that atmospheric CO_2 lowering in the glacial episodes was caused by sequestration in a poorly ventilated, dense, cold deep water layer.