

## New interpretations on Liesegang ring-like structures in petrology

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This paper presents new interpretations on genesis of Liesegang ring-like structures in petrology. Examples of Liesegang ring-like structures in rocks are (1) periodic precipitates of iron hydroxide in hydrothermally altered rhyolite, (2) banded skarn between marble and granodiorite, and (3) a particular example of igneous layering from Bilibili alkaline intrusion, Sulawesi, Indonesia.

The key features of the Liesegang ring are periodic appearance of precipitates (rings) and the spacing law for the periodicity of the rings. The standard theory of the Liesegang ring at present is the supersaturation theory incorporating competitive particle growth (Ostwald ripening) model (e.g. Freney et al.:1983). My new interpretations are based on a consideration of constraints on thermodynamic forces and their conjugate fluxes, which are not fully incorporated into the existing theory.

First I will discuss a classical example of a Liesegang ring in  $\text{AgNO}_3$  - HCl system. Electrical neutrality condition gives a constraint on diffusive fluxes in this case. I assume that diffusion of  $\text{H}^+$  is much faster than those of other species. Uphill diffusion of  $\text{Cl}^-$  occurs due to the electrical neutrality condition if diffusivity of  $\text{NO}_3^-$  is larger or smaller than that of  $\text{Ag}^+$ . The position of the ring formation is determined by that of the peak of  $\text{Cl}^-$  according to the supersaturation theory. This interpretation will be applicable to the example (1).

Secondly I will discuss more general situations in which the Gibbs - Duhem relation and the volume - fixed reference frame (a kind of conservation law) will give linear couplings among thermodynamic forces and fluxes, respectively. In such a case uphill diffusion can take place in a multicomponent system even for ideal solution (Nishiyama, 1998). As discussed by Nishiyama (1994), uphill diffusion will play a major role in formation of metamorphic layering. Similarly, uphill diffusion due to the linear couplings may cause Liesegang ring-like structure in banded skarn.

Finally I will discuss the origin of Liesegang ring-like structure in igneous layering from the same point of view.

### References

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## N and Ar isotopes of fluid inclusion in Early Archean agate from North Pole area, Pilbara craton, West Australia

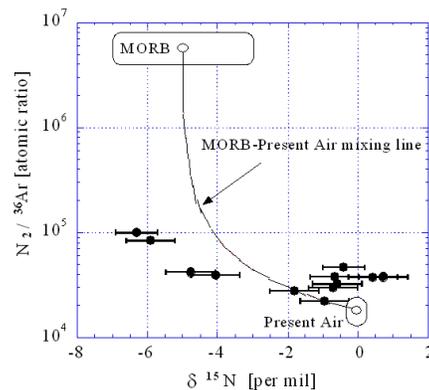
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Recently, carbonaceous filamentous structures were found in the Archean kerogen-rich silica dikes that have intruded basaltic greenstones from North Pole area in the Pilbara craton, West Australia. The origin of kerogen is debated. Some kerogen in the silica dykes contain N with C/N atomic ratio of ~200 (Ueno, personal communication).

Here, we report N isotopic compositions for fluid inclusions in agate associated with the silica dikes, in order to evaluate the origin of fluid components and kerogen by investigating the relation between N from fluid components and that from kerogen. Peaks of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  were identified by Raman microspectrometry of the fluid inclusions. Crushing experiments showed that  $\delta^{15}\text{N}$  values and  $\text{N}_2/^{36}\text{Ar}$  ratios for the fluid components are  $-6 \sim 0\text{‰}$  and  $2.2 \times 10^4 \sim 9.9 \times 10^4$  respectively. If these values for modern upper mantle ( $-5 \pm 2\text{‰}$ ,  $6 \pm 2 \times 10^6$ ) and air ( $0\text{‰}$ ,  $1.8 \pm 0.7 \times 10^4$ ) (Sano et al., 1998) are applicable to Early Archean samples, N in the fluid inclusions can be explained by mixing of contemporary upper mantle and air. In addition,  $\delta^{15}\text{N}$  values for the fluid components can partly explain those of the kerogen ( $-4 \sim 4\text{‰}$ ; Ueno, personal communication). Since N isotopic fractionation associated with biological  $\text{N}_2$  fixation is small ( $-1 \sim 2\text{‰}$ ; Wada, 1980), it may be possible that the origin of N in the kerogen is biologically fixed  $\text{N}_2$  from contemporary fluid.



**Figure 1.** A correlation diagram between  $\delta^{15}\text{N}$  values and  $\text{N}_2/^{36}\text{Ar}$  ratios for the fluid inclusions in agate.

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