# Methane, an important component of fluids in graphitic metapelites

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#### Introduction

Graphitic metapelites make-up significant portions of convergent orogens. Thermodynamic models predict that graphite should react with water in medium and high-grade metamorphic rocks to generate carbonic fluid species, but their proportion should be small and there should be equal amounts of  $CO_2$  and  $CH_4$ , unless the ratio is externally controlled (e.g., Connolly and Cesare, 1993).

We analyzed isotopic composition and crystallinity of disseminated and vein graphite as well as fluid inclusion compositions in quartz veins found in metasedimentary rocks in the Black Hills, South Dakota, to determine the composition of fluids that were generated during metamorphism associated with the Trans-Hudson orogeny and intrusion of the lateorogenic Harney Peak Granite.

### **Evidence for methane**

Both disseminated graphite and graphite precipitated in quartz veins and selvages within the granite contact aureole show high degree of crystallinity, as revealed by Raman spectroscopy.  $\delta^{13}$ C values of disseminated graphite range from –27.5 to –20.8‰. There is a weak negative correlation of the  $\delta^{13}$ C values with the total amount of graphite in the whole rocks (i.e., the lower the abundance of graphite, the less negative its  $\delta^{13}$ C). This correlation is attributed to reaction of organic matter and/or graphite to methane. The vein graphite has  $\delta^{13}$ C of about –17‰ the selvage graphite has about –22‰. These compositions are best explained by progressive precipitation of graphite from a methane-rich fluid as it passed from veins to the host rocks. The presence of methane in the fluid is supported by early methane-rich fluid inclusions in quartz veins.

#### Conclusions

This study shows that methane is likely to be an abundant carbonic component in large pelitic terranes undergoing metamorphism during collisional orogenies. A high  $CH_4/CO_2$  ratio in the fluid may be the results of early decomposition of organic matter during incipient metamorphism and subsequent buffering by metamorphic reactions (c.f. Ohmoto & Kerrick, 1977).

#### References

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## Stability of forsterite, enstatite, and silicate melt around young and evolved stars

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Recent finding of crystalline forsterite and enstatite around evolved and young stars [1-4] suggests common ocurrence of crystalline silicates in wide conditions of stellar environment. The fitting of IR spectra from young and evolved stars to laboratory measured one shows significantly low temperature (~100K) of the crystals and more abundance of enstatite than forsterite for circumstellar environments. Amorphous silicate is also estimated to be present around crystalline silicates in circumstellar discs. Amorphous silicates are generally estimated to be "astronomical silicate", which is a mixture of amorphous Mg-Si silicate and fine-grained metal particles to explain high opacity [5].

The question arises is how the crystalline nature of the silicate dusts was achieved and in what conditions they were formed. The stability of forsterite and enstatite was extensively studied by [6], however, they did not take the presence of Ca and Al into consideration, which should affect the stability of silicate melt at certain physical conditions. The full investigation of multi-component system was studied for the solar nebula by [7], however, the difference in bulk composition, particularly less relative abundance of hydrogen in O-rich environment of evolved stars is quite different from the solar nebula conditions. In the present study, we study the stability of forsterite, enstatite, and silicate melt in a wide range of pressure, temperature, and composition conditions.

The system studied is mulit-components with various H to other element ratio and various C/O ratio, the pressure ranges from  $10^{-10}$  to  $10^{-4}$  bar, and temperature ranges from 1000 to 2500K. The results show fairly large stability of silicate melt at high P-T and high O/C conditions. The results suggest that formation of abundant enstatite requires chemical fractionation due to earlier condensation of forsterite at higher temperature region to form Si-rich gas and that "amorphous" silicate can be either quenched silicate melt formed at relatively high P-T conditions or fractionated gas that became Si-rich due to earlier forsterite condensation, which is the same process as that responsible for enstatite formation. Further investigation including kinetic processes is undergoing.

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