

Phengite buffering of mineral reactions in HP–LT metapelites

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The (Si⁴⁺) content of phengites has been widely used in petrology as a powerful geobarometer indicative of high pressure (HP) metamorphism. On the other hand, the literature abounds with phengite analyses of variable interfoliar K content. Interfoliar cation content in natural phengites is indeed frequently < 1 p.f.u. (Guidotti, 1984). While some studies have shown that this variability could be accounted by the presence of vacancies or hydronium ions, much less studies have concentrated on the information one may retrieve from it. Previous studies have essentially pointed to the importance of the role of temperature on the increase of the interfoliar K content with diagenese, incipient metamorphism (Hunziker *et al.*, 1986), low- to middle-grade metamorphism (Wang and Banno, 1987).

Important variations in the K content of phengites are encountered in HP–LT environment too. A few microprobe analyses suffice to evidence such variations in the 'Schistes Lustrés' of the Franco-Italian Western Alps. From a fluid inclusion and petrological study on this 'Schistes Lustrés' domain, Agard *et al.* (submitted) suggested that phengites, the only K-bearing minerals in these metapelites, might play a significant role in the observed limited alkali variations of the fluid phase throughout the recorded metamorphic evolution. This is echoing recognition by Walther and Orville (1986) that phyllosilicates might serve as sensitive indicators of fluid:rock interaction. To test this hypothesis, we therefore performed an analysis of a large number of natural phengites, including retrograde phengites formed as carpholite breakdown products.

Variations of the phengitic composition

In the 'Schistes Lustrés' domain, parageneses indicate a continuous evolution from prograde blueschist facies (BS) early metamorphic conditions to retrograde greenschist facies (GS) overprint. Estimated PT conditions for the BS stage range from around 13 kbar and 380°C in the west to 20 kbar and 450°C in the east (Agard *et al.*, submitted). Metamorphic conditions are notably documented by

the index HP mineral carpholite, found in great amounts in the western area. In the eastern domain, carpholite crystals are replaced by chloritoid and only remain as relics in quartz. Phengites are found replacing both minerals and chlorite is widespread. Figure 1 shows microprobe data for 180 phengites selected with respect to associated parageneses (notably carpholite occurrences), size, microtextural and tectonic position. Three sort of phengites were analysed: 1) HP phengites – 'A' – associated with and cogenetic with carpholite relics in quartz, 2) retrograde phengites – 'B' – replacing carpholite (essentially encountered in the western part of the 'Schistes Lustrés', 3) phengites – 'C' – associated to or replacing chloritoid (found in the east).

Phengites, which are very close to the ideal $\text{SiR}^{2+}\text{Al}_2$ -tschermak substitution, evidence a clear difference between two variation trends: large K (B-

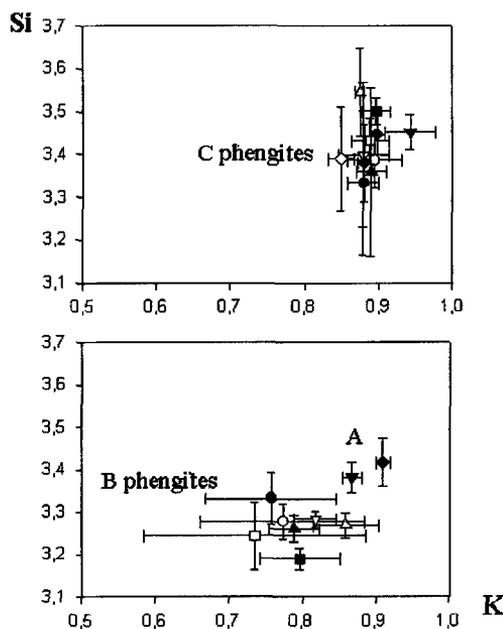


FIG. 1. Si vs K content of phengites (19 rock samples).

type phengites) or large Si variations (C-type phengites). Eastern samples display a coherent drop of tschermak Si content as retrogression proceeds, from 3.5 to 3.25–3.3 on average. While retrograde phengites associated to carpholite show a largely variable K content (from 0.67 to 0.93 in individual samples), it should be underlined that relic prograde phengites have intermediate characteristics (high interfoliar K content and Si content) between B and C samples. Retrograde phengites clearly have a lower K content than the earlier (HP relic) phengites. In addition, retrograde phengites show a decreasing K content with time: phengites replacing carpholite pseudomorphs aligned and stretched on the schistosity predate bud-like phengites replacing carpholite crystals isolated in quartz. Finally, it should be noted that where carpholite did not crystallize in significant amounts during the metamorphic evolution, the – westernmost; inherited? – phengites were left with a relatively high K content.

Discussion

Of major interest is the retrograde K content decrease in carpholite associated phengites. It can be accounted by a combination of: (1) massive water release related to the carpholite breakdown and large enough fluid:rock ratios to drive away and transport significant amounts of alkali (i.e. 15–20%). This is probably not very important since GS inclusions are very dilute and homogeneous (Agard *et al.*, *subm.*); (2) limited amount of overall available K from the HP phengites; but alkali were not significantly concentrated during HP water production (Agard *et al.*, *subm.*) and relict phengites in the schist were therefore probably close to maximum K content; (3) apparent dilution by the breakdown product pyrophyllite. The small scale solution or mixture of phengite and pyrophyllite would result in a lowering of the K content with time. Mixing of 15–20% pyrophyllite with the low-Si phengites from the eastern samples (supposedly representative of the common phengitic composition in most retrograde greenschist facies) yields phengite compositions consistent with phengitic compositions observed in

carpholite pseudomorphs. This breakdown reaction might proceed from the reaction $Cp + Qtz \rightarrow Prl + Chl$ rather than $Cp + Qtz + Phg 1 \rightarrow Chl + Phg 2$ as suggested by Agard *et al.* The lowering of 15–20% of the K content of phengites (Fig. 1), which relates to 15–20% of pyrophyllite, is in first approximation consistent with the quantitative estimates of the total amount of carpholite produced during prograde reactions, as deduced from outcrop (Agard *et al.*, *subm.*).

Conclusion

Some features of the interfoliar K content are clearly independent of the whole rock chemistry. It is demonstrated that although temperature plays an important role, K content is also controlled by mineral reaction and/or fluid:rock interaction. In light of the results and in the absence of yet reported adequate precursor forming carpholite (no pyrophyllite was found and rocks are far too ferrous to contain sudoite; see Goffé and Vidal, 1992), we propose that prograde – low K content, ‘illitic’ – phengites are responsible for the formation of carpholite. This reaction would thus have been operative throughout both the prograde and the retrograde PT evolution. Finally, one should insist on the importance of phyllosilicates as mineral buffers, as illustrated by the very adaptable composition of these low- to medium-temperature HP phengites.

References

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