

### Abstract

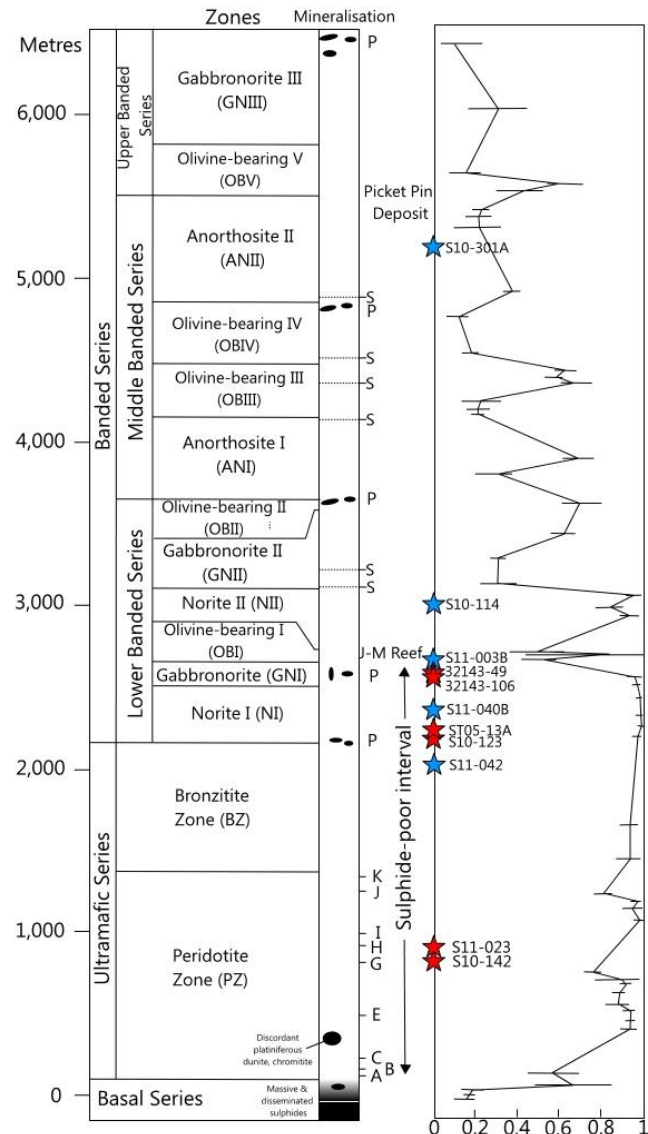
The processes involved in the petrogenesis of the sulphide-hosted platinum-group-element (PGE) deposits of the Stillwater Complex are controversial, with theories ranging from orthomagmatic to hydromagmatic. To further constrain these models, we have been examining the trace phase assemblages in rocks away from the ore zones.

High-temperature carbonates have been observed in association with sulphide minerals below the platiniferous J-M Reef of the Stillwater Complex. The carbonate assemblage consists of dolomite with exsolved calcite and is found in contact with sulphide minerals: chalcopyrite and pyrrhotite in the Peridotite Zone; and pyrrhotite with pentlandite, pyrite and chalcopyrite in Gabbronorite I of the Lower Banded Series.

The minimal silicate alteration and the lack of greenschist minerals in association with the mineral assemblage are consistent with a high-temperature origin for the carbonates. The calcite-dolomite geothermometer yields a minimum formation temperature of ~950°C for the unmixed assemblages. The carbonate assemblages are consistent with Stillwater fluid inclusion studies, showing that fluids comprising coexisting Cl-rich brine and carbonic fluid were trapped in pegmatic quartz at 700–715°C, some of which also contained “accidental” calcite inclusions. The high Cl-content of apatite found below the platiniferous J-M Reef is further evidence that a Cl-rich fluid was migrating through the rocks beneath the Reef. Carbonates have been shown to be stabilized by Cl-rich fluids.

The association of high-temperature carbonates with sulphides beneath the J-M reef supports the hydromagmatic theory which involves a late-stage chloride-carbonate fluid percolating upwards, dissolving PGE and sulphides and redepositing them at a higher stratigraphic level.

This research has implications for the formation of platinum-group-element (PGE) rich deposits as it provides further support for the presence of high temperature Cl- and carbonate-bearing fluids, which have been shown to be capable of remobilising sulphides, PGE and chalcophile elements. This suggests the involvement of fluid not only in the formation of the Stillwater Complex’s J-M reef but also of analogous deposits worldwide and could provide a new tool for PGE exploration.



**FIGURE 1:** Stratigraphy of the Stillwater Complex, showing occurrences of sulphide pods (S), chromitite bands (A-K), the J-M Reef (labelled) and the Cl/(Cl+F) ratio of apatites. Also shown are occurrences of high temperature (red stars) and low temperature (blue stars) carbonates. Note that only low temperature occurrences are found above the reef, where both high and low temperature carbonates are found below the reef. After Boudreau et al. (1997).

# High-temperature Carbonates in the Stillwater Complex, Montana, USA.



Complex, Montana, USA.

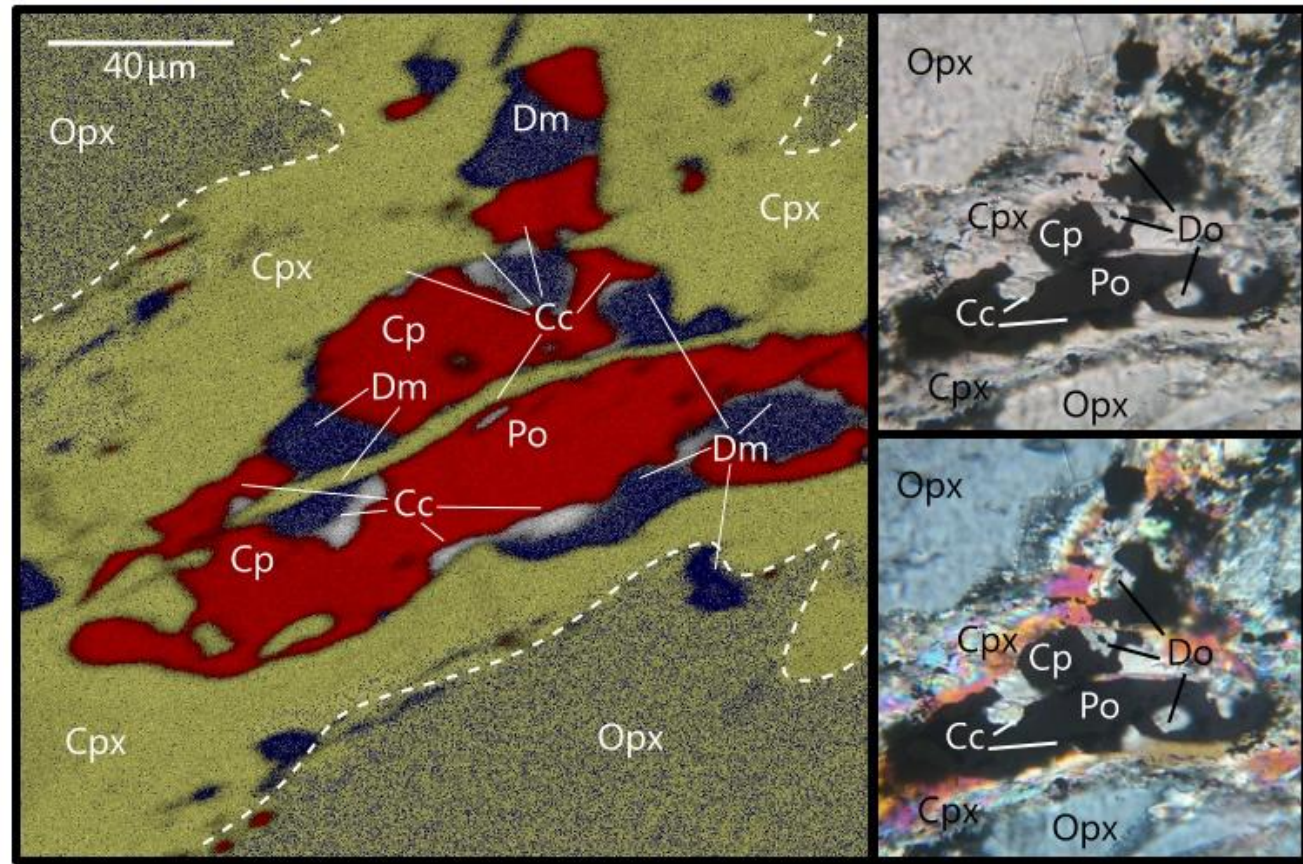


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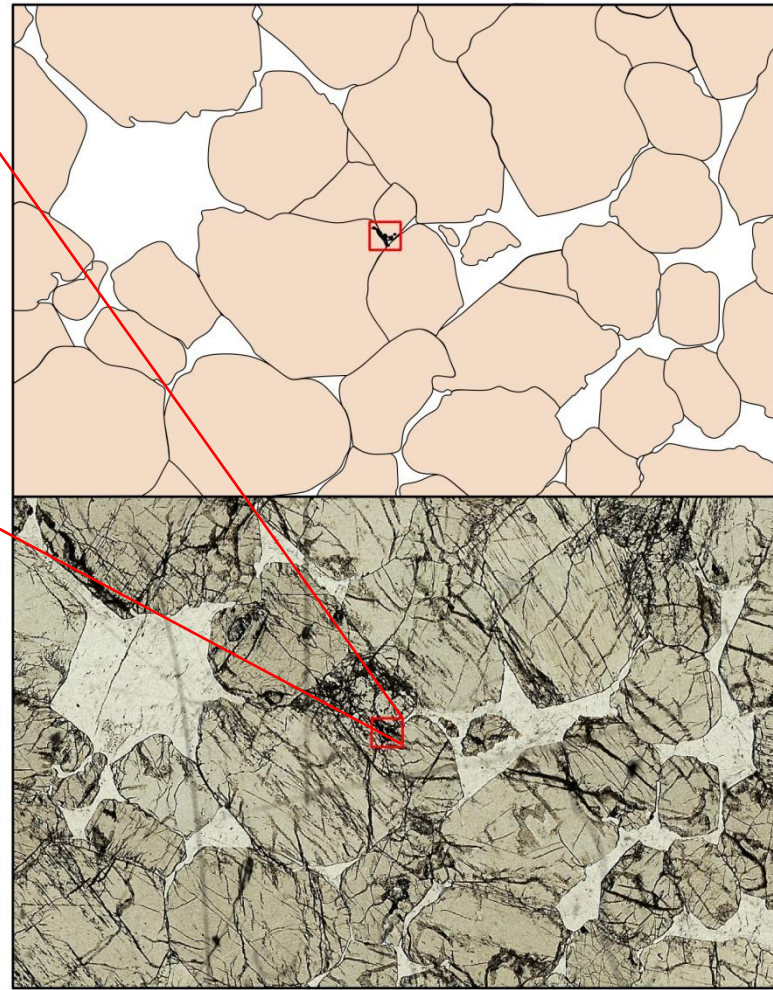
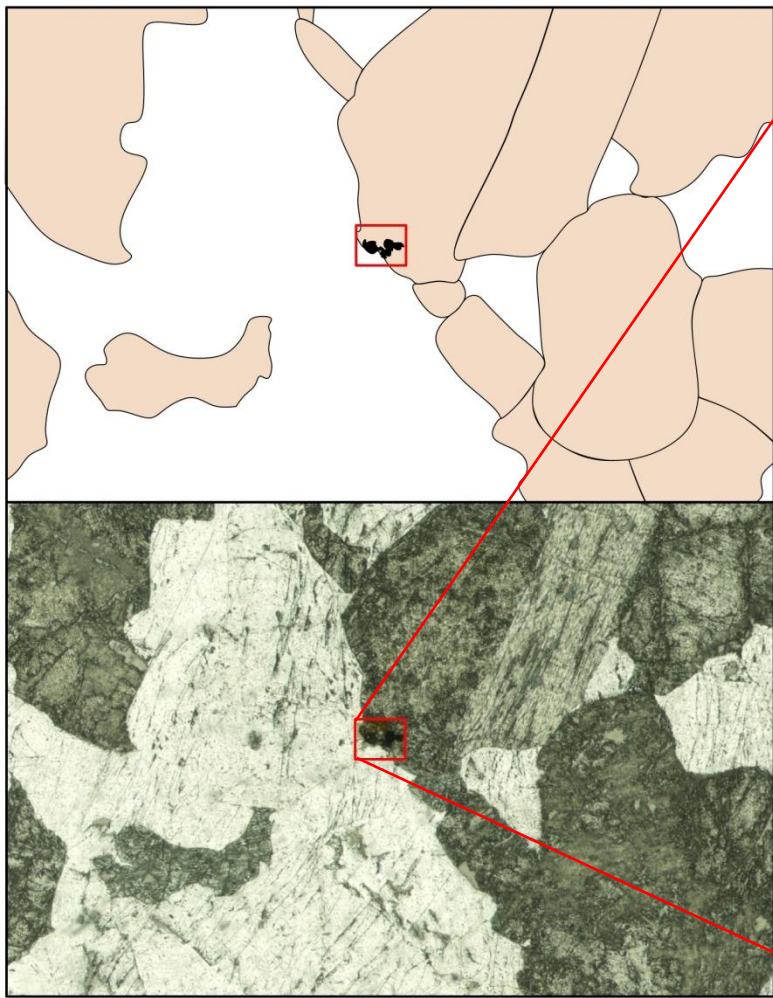
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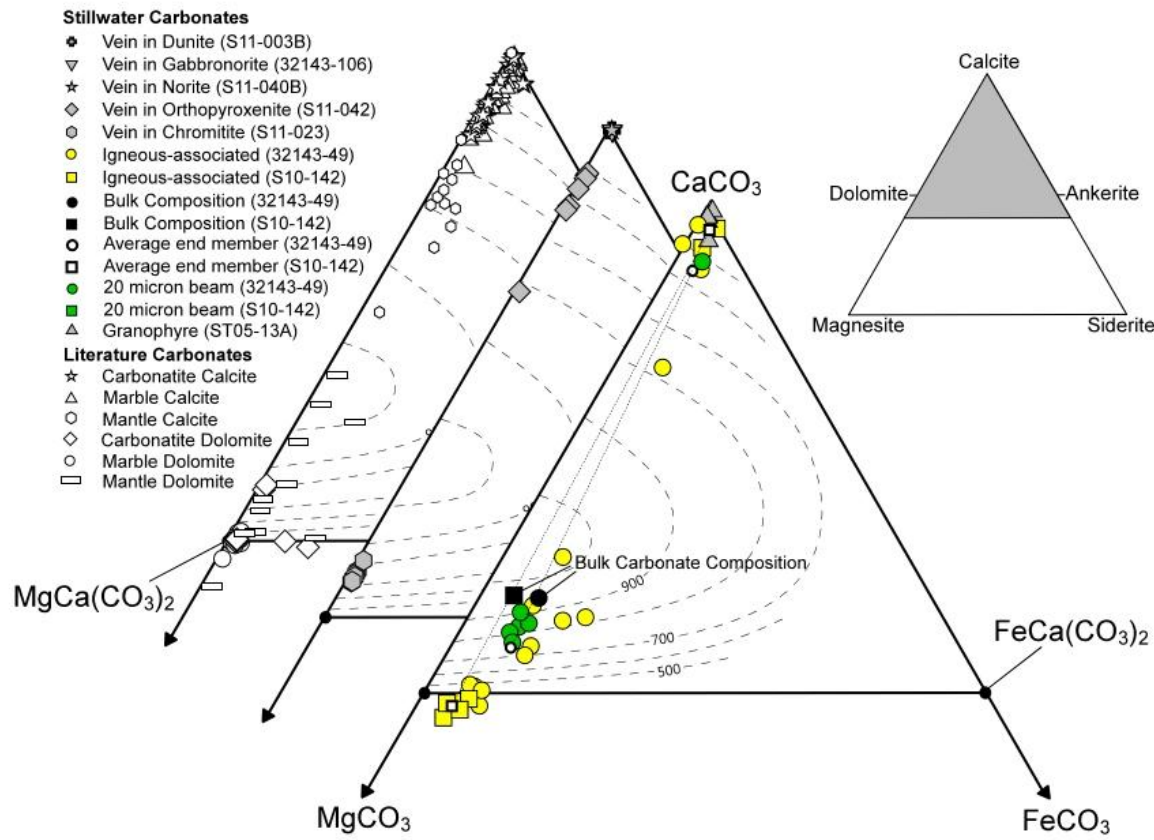
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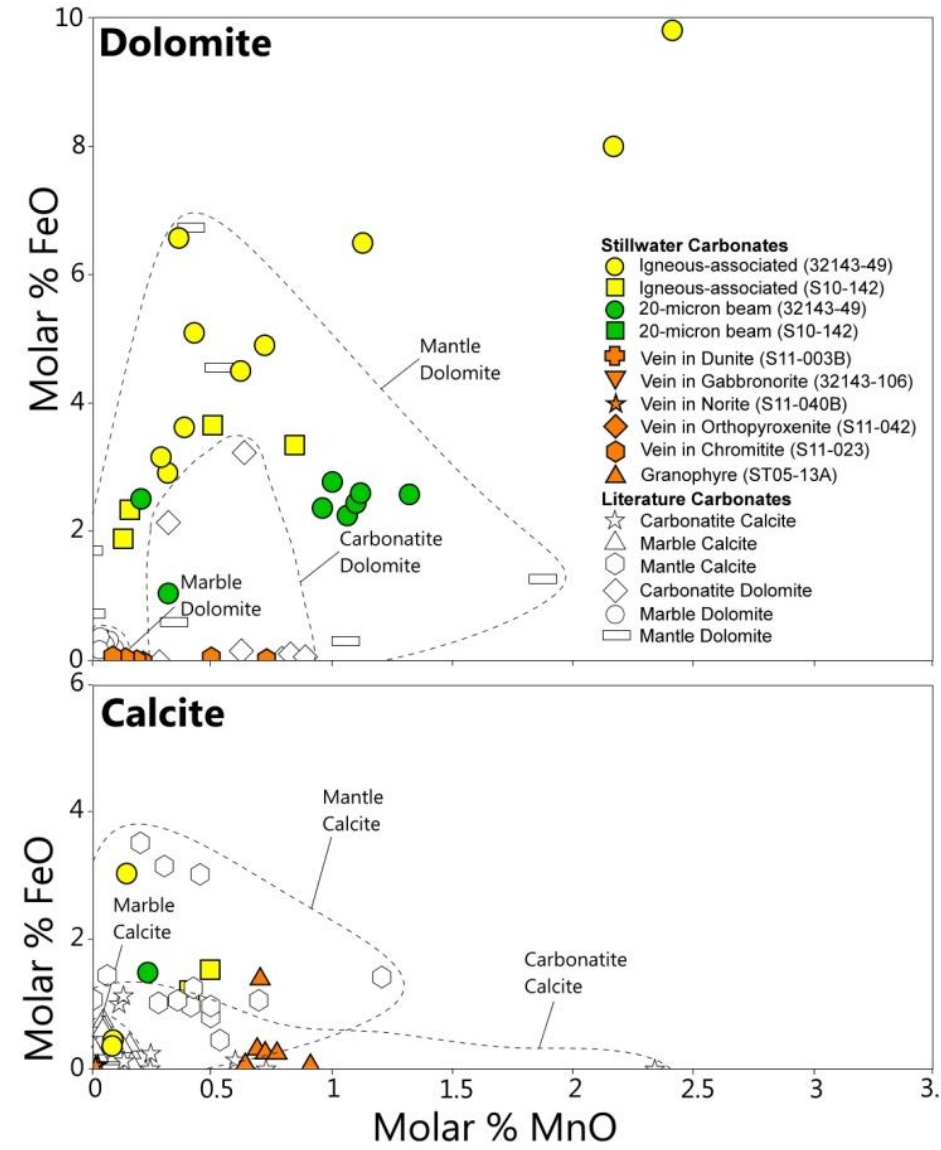
**FIGURE 3:** Phase map of sample 32143-49 (gabbronorite zone I) showing patchy nature of exsolution in high-temperature carbonates. Also demonstrates their relationship with quartz, sulphides, fresh plagioclase and the Ca-rich pyroxene rim. Abbreviations: Opx orthopyroxene; Cpx clinopyroxene; Dm dolomite; Cc calcite; Po pyrrhotite; Qtz quartz; Plag plagioclase feldspar. Dashed white line to outline the reaction rim of clinopyroxene between the orthopyroxene and the carbonate-sulphide assemblage.



**FIGURE 2:** Phase map of sample S10-142 (peridotite zone) showing high-temperature carbonates and their relationship to sulphides and pyroxenes. Abbreviations: Opx orthopyroxene; Cpx clinopyroxene; Dm dolomite; Cc calcite; Po chalcopyrite; Po pyrrhotite. Dashed white line to outline the reaction rim of clinopyroxene between the orthopyroxene and the carbonate-sulphide assemblage.



**FIGURE 4:** Carbonate ternary diagrams displaying the composition of carbonate occurrences from both the Stillwater Complex and the literature (after Anovitz & Essene, 1987). The bottom plot shows literature data; the middle plot shows Stillwater vein data; and the upper plot shows Stillwater igneous (sulphide-associated and granophyre) data. The igneous data show a much greater range in Fe-content than the vein data.



**FIGURE 5:** Plot of molar % FeO against molar % MnO for calcite and dolomite occurrences from the Stillwater Complex with literature data fields for comparison. Most Stillwater vein data lie within the same range as the marble data fields. Most Stillwater igneous data extend past the carbonatite data fields. The granophyre data shows significant overlap with the carbonatite calcite data field.

### Conclusions

High-temperature carbonates have been found showing exsolution of calcite from a more dolomitic carbonate. These assemblages are found in association with sulphide minerals. The surrounding silicates show a lack of greenschist alteration, but a Ca-rich pyroxene rim is found at the contact of the carbonate-sulphide assemblage with its orthopyroxene host. This is also seen at the contact of mantle carbonates with their host silicates and is suggested to represent unstable phases intermediate in the transition from orthopyroxene to true clinopyroxene.

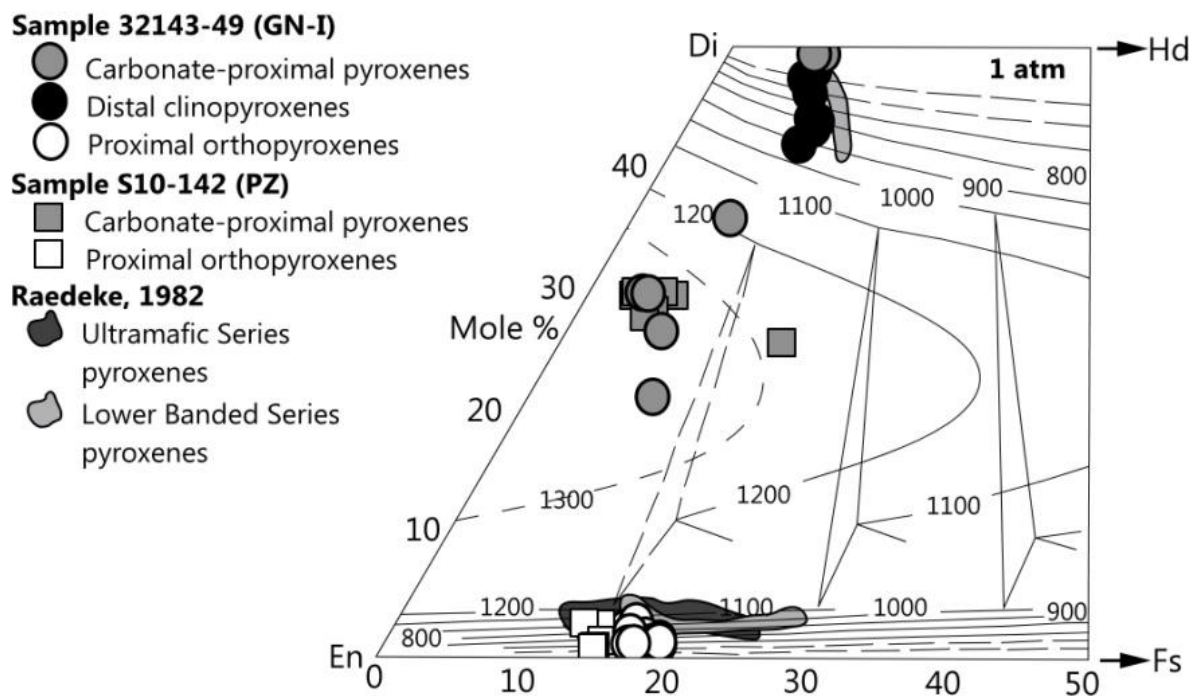
The carbonates show a compositional overlap in terms of MnO and FeO with mantle carbonates, and show much higher MnO and FeO contents than other Stillwater carbonates, including vein carbonates from BZ, N-I, OB-I and N-II. The compositions of the host ortho- and clinopyroxenes and of the Ca-rich pyroxenes are consistent with an igneous temperature of formation. The high-temperature carbonates are associated only with the Cl-rich section of the Stillwater Complex and are closely associated with sulphides in an otherwise S-poor portion of the stratigraphy, suggesting that the formation of the sulphides and carbonates in this section may be related.

The association of high-temperature carbonates with sulphides beneath the J-M reef supports the hydromagmatic theory which involves a late-stage chloride-carbonate fluid percolating upwards, dissolving PGE and sulphides and redepositing them at a higher stratigraphic level. Carbonate-Cl fluids are believed to be effective in transporting PGE (e.g. Kanitpanyacharoen & Boudreau, 2012).

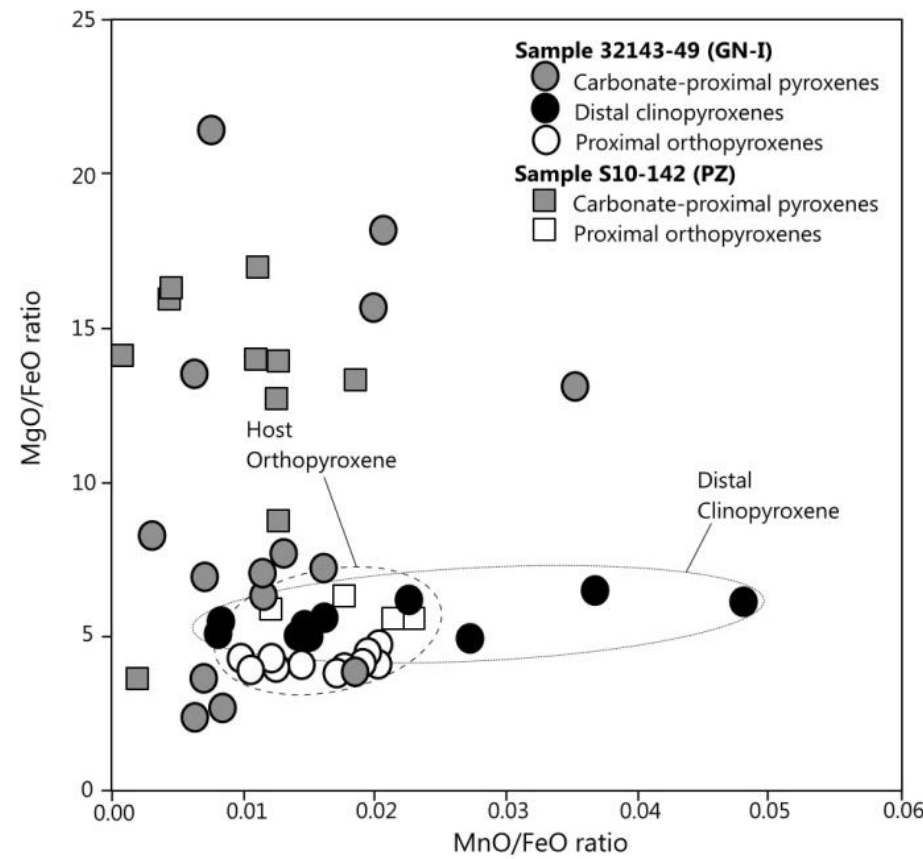
### References

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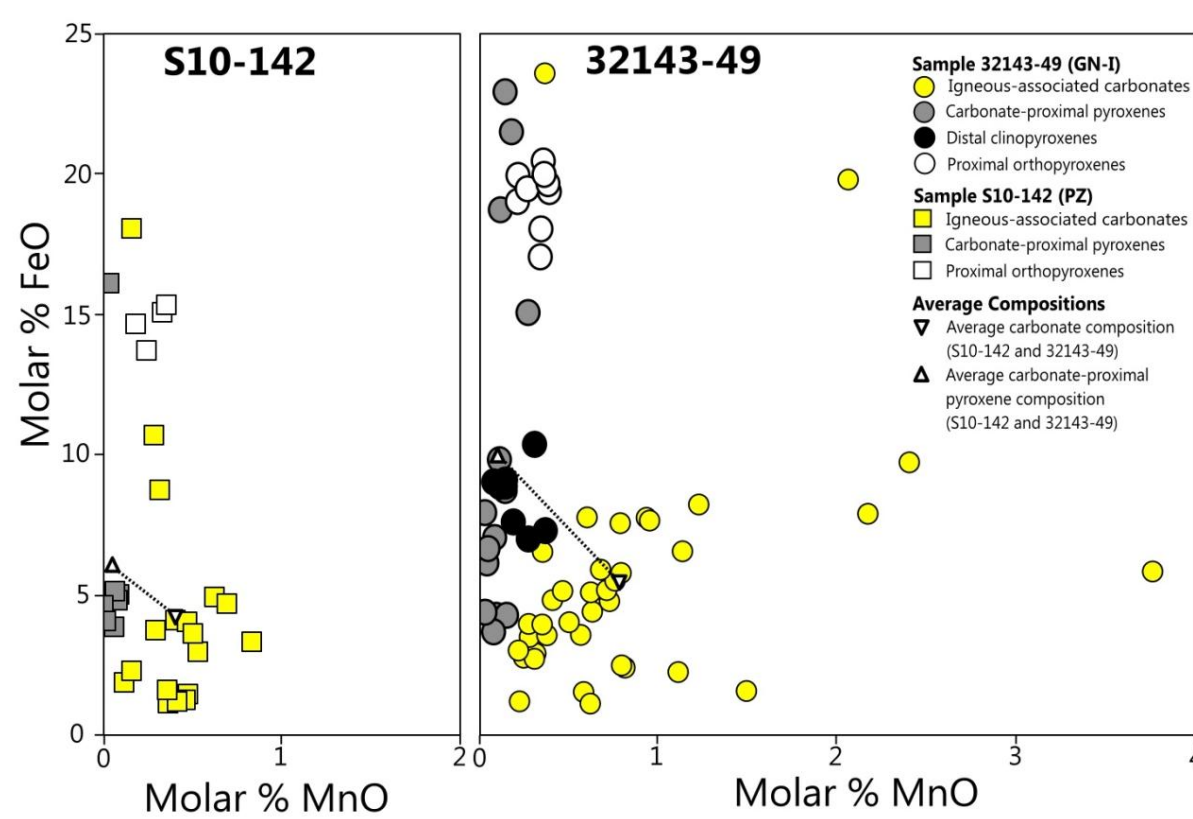
### Acknowledgements



**FIGURE 6:** Pyroxene compositions from GN-I and PZ are plotted onto the diopside – hedenbergite – ferrosilite – enstatite quadrilateral contoured for temperature (Lindsley and Andersen, 1983). Compositional fields for pyroxenes from the ultramafic and lower banded series (Raedeke, 1982) are shown for comparison.



**FIGURE 7:** Plot of pyroxene ratios MnO/FeO ratios are plotted against the MgO/FeO ratios of pyroxenes from GN-I and PZ (after Nakano et al 1994).



**FIGURE 8:** Plot of MnO against FeO for pyroxenes and carbonates. The MnO and FeO contents of pyroxenes from GN-I and PZ and carbonates from PZ, BZ, N-I and GN-I are plotted. Distal clinopyroxenes, host orthopyroxenes, granophyre carbonates and carbonate veins through chromitite, norite, orthopyroxenite and dunite are all plotted as compositional fields. Sulphide-associated carbonates are plotted as yellow symbols and carbonate-proximal pyroxenes as grey symbols.