Electronic Annex EA-1 (figures):

Evidence for free oxygen in the Neoarchean ocean based on coupled iron–molybdenum isotope fractionation

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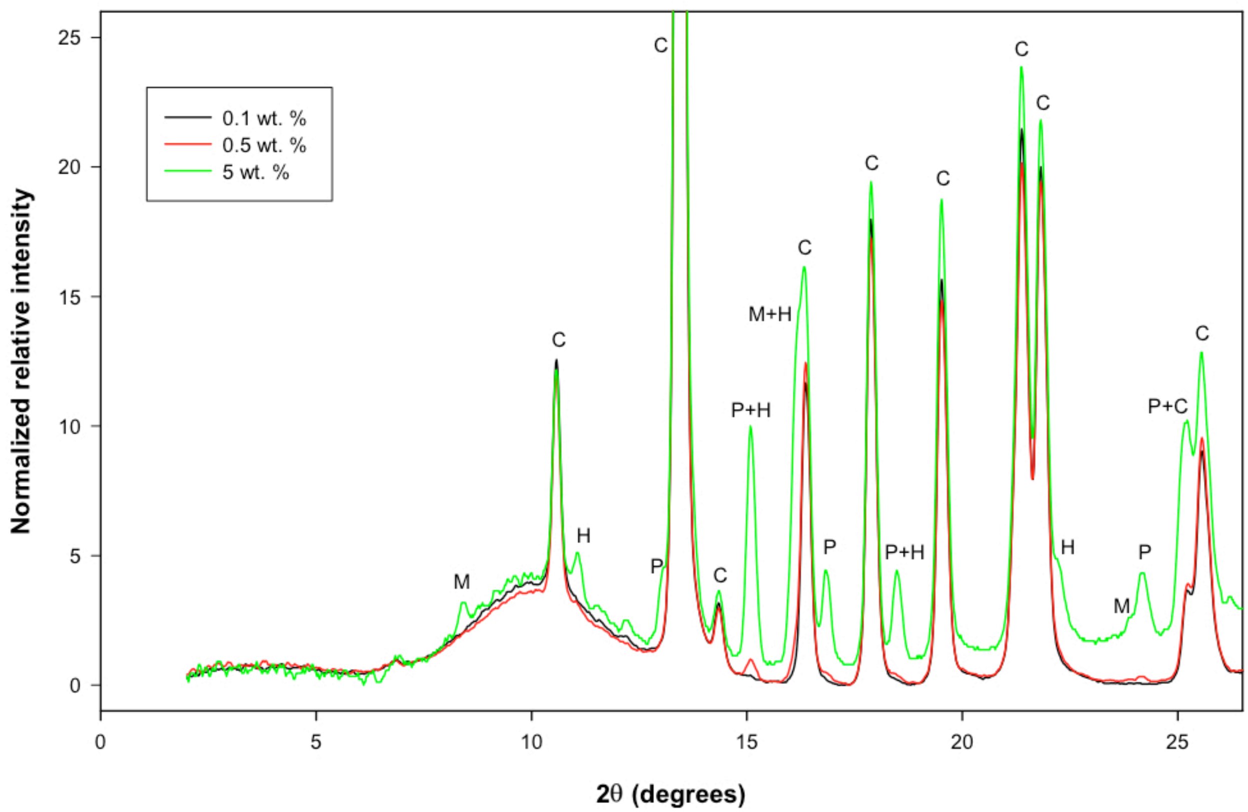
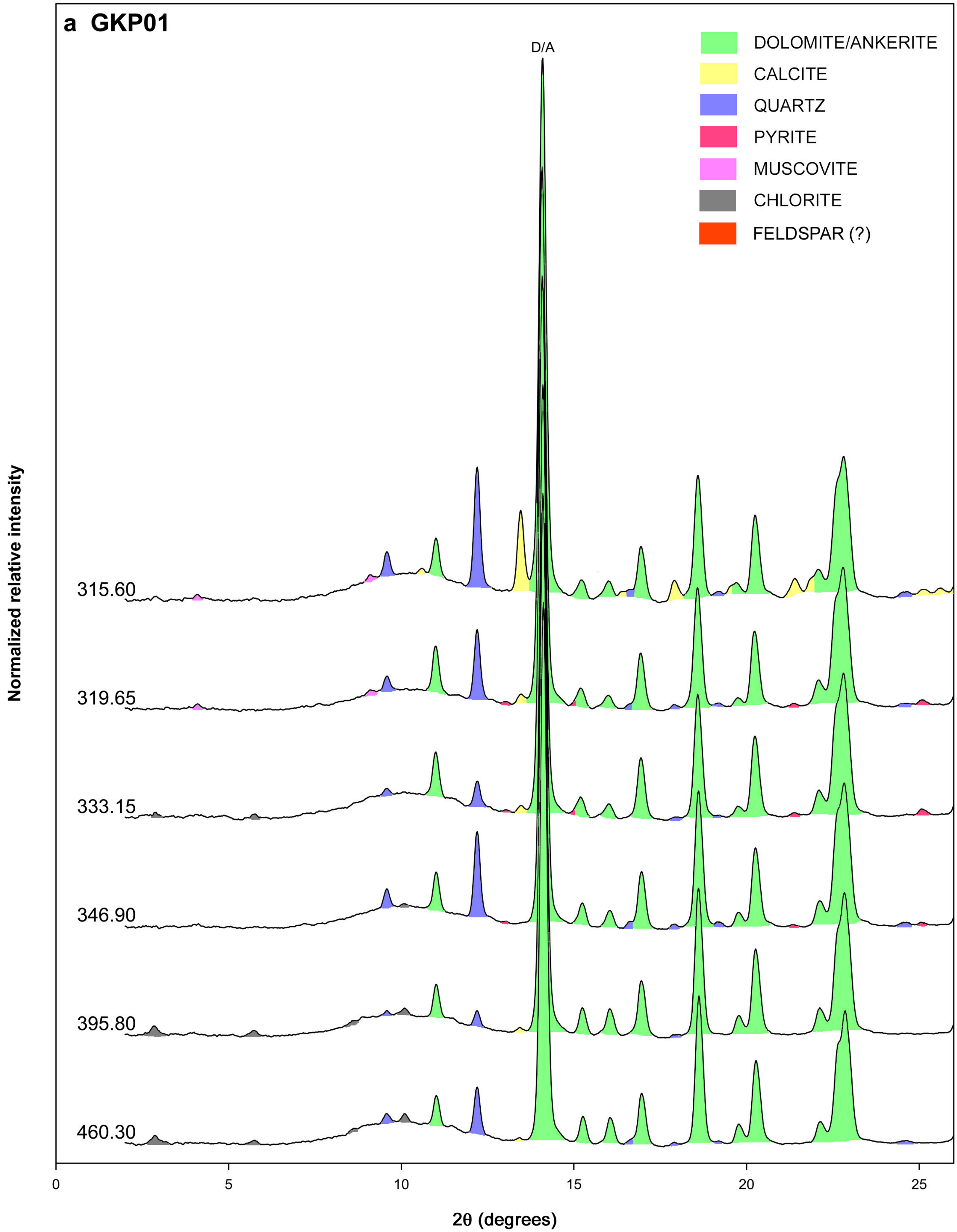
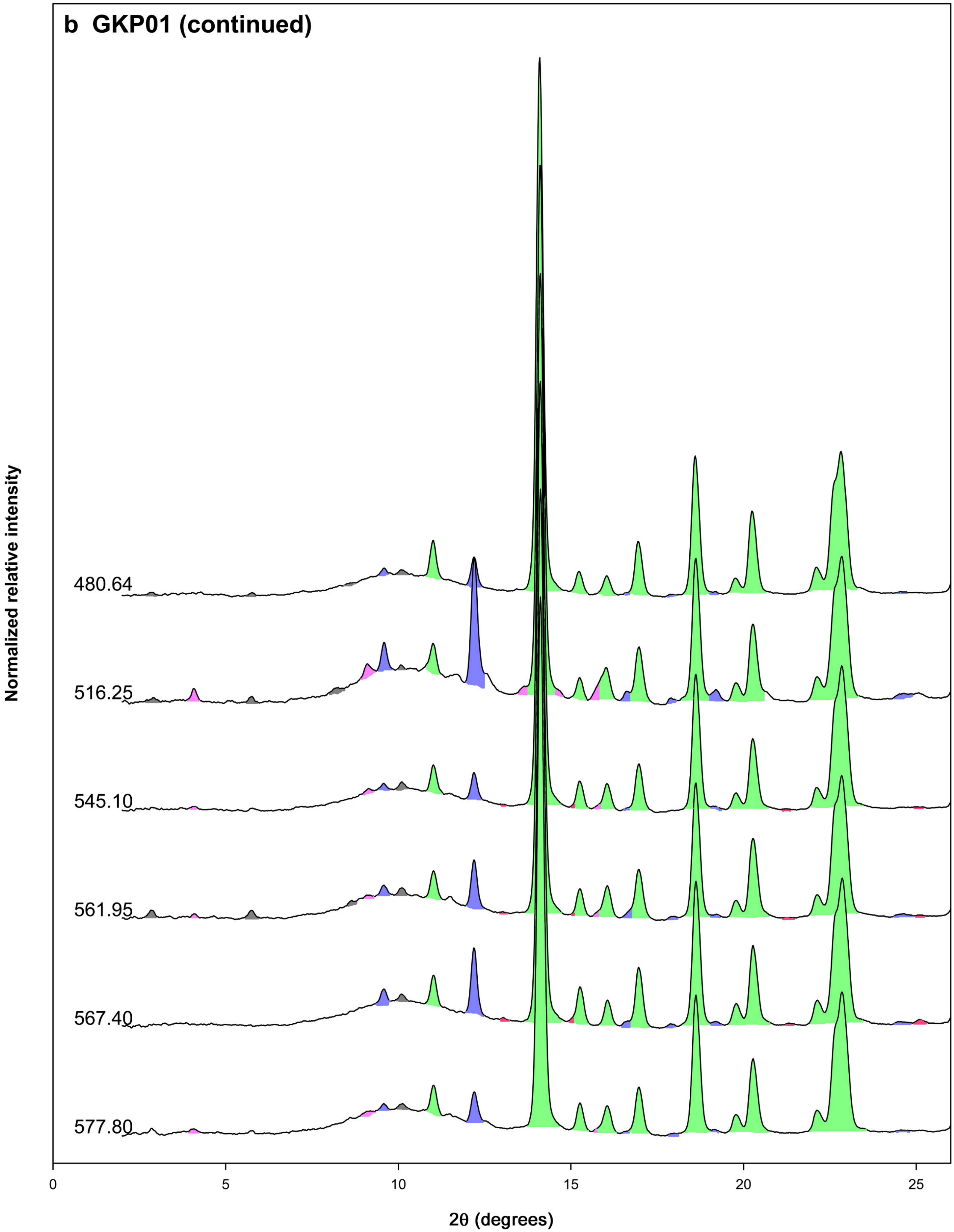
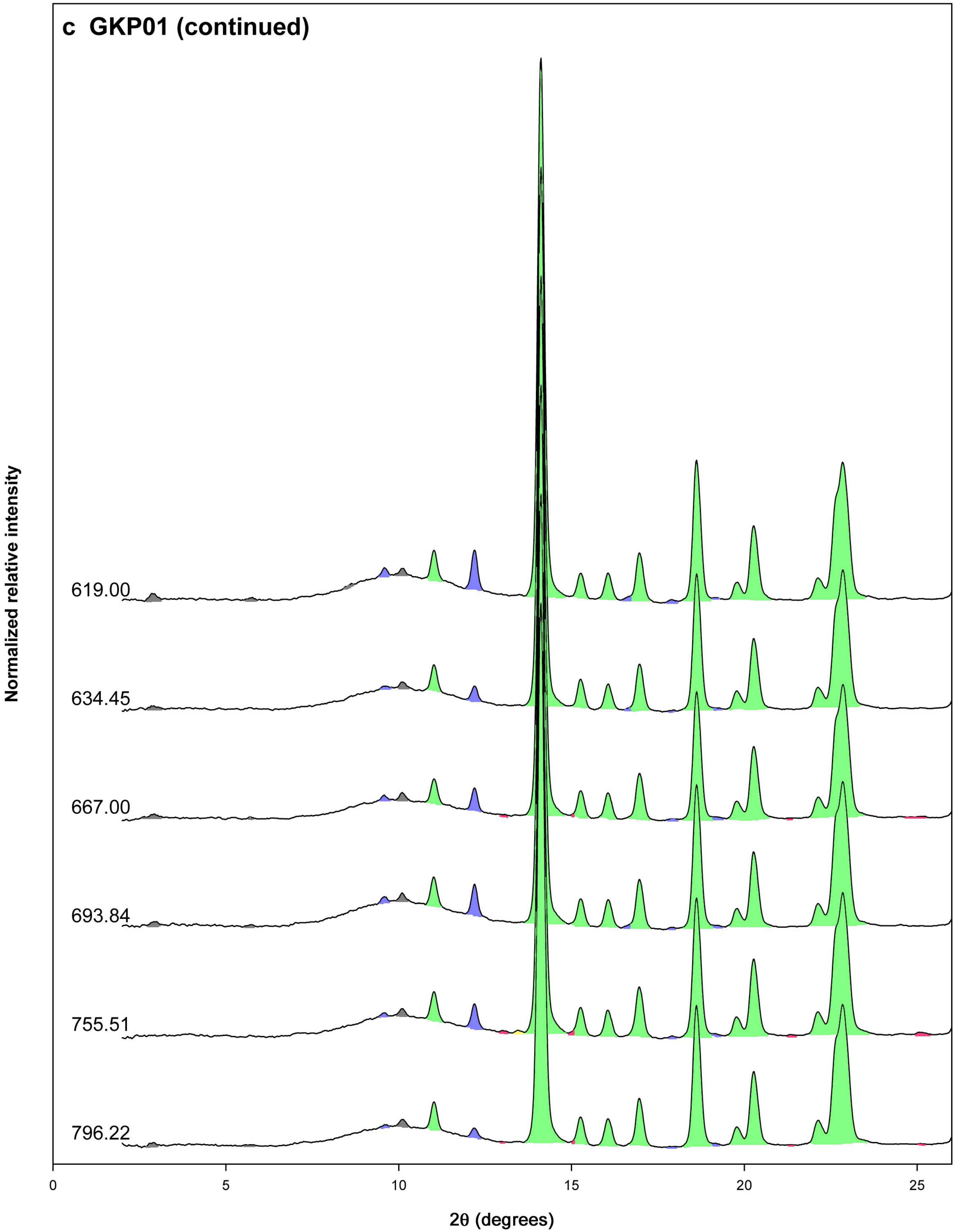


Figure EA-1-1. XRD paterns of test mixtures of calcite (C) , hematite (H), magnetite (M), and pyrite (P) powders of various proportions; 0.1 wt.% signifies a mixture of 99.7 wt.% calcite and 0.1 wt.% of each of the other phases, 0.5 wt.% signifies a mixture of 98.5 wt.% calcite and 0.5 wt.% of each of the other phases, and 5 wt.% signifies a mixture of 85 wt.% calcite and 5 wt.% of each of the other phases. The spectra have been normalized to the [1 0 4] peak of calcite at 13.419º, which has an intensity of 100 on this scale. No baseline subtraction was performed.

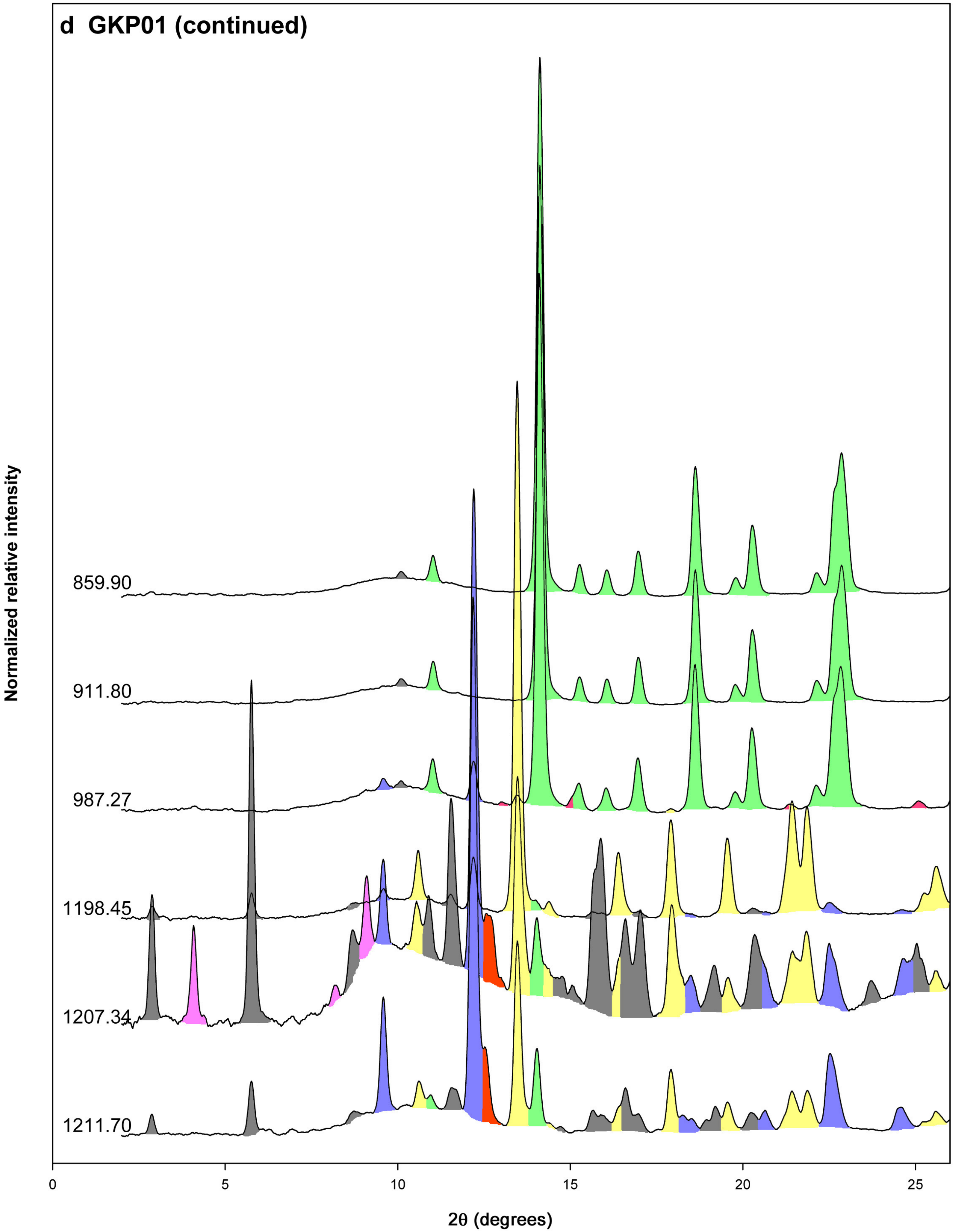

a GKP01
D/A
DOLOMITE/ANKERITE
CALCITE
QUARTZ
PYRITE
MUSCOVITE
CHLORITE
FELDSPAR (?)
315.60
319.65
333.15
346.90
395.80
460.30
Normalized relative intensity
0
5
10
15
20
25
2θ (degrees)

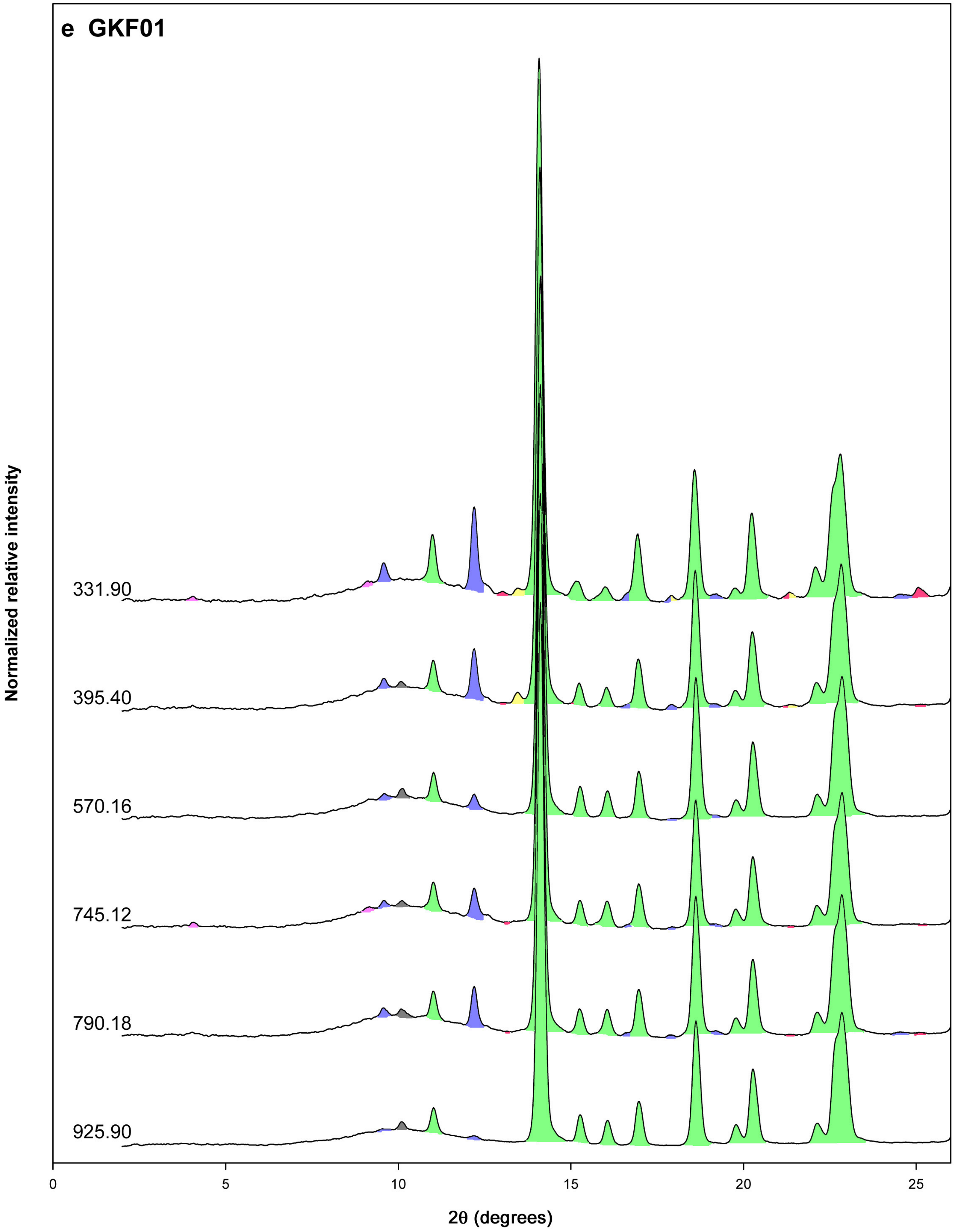


b GKP01 (continued)
Normalized relative intensity
480.64
516.25
545.10
561.95
567.40
577.80
0
5
10
15
20
25
2θ (degrees)

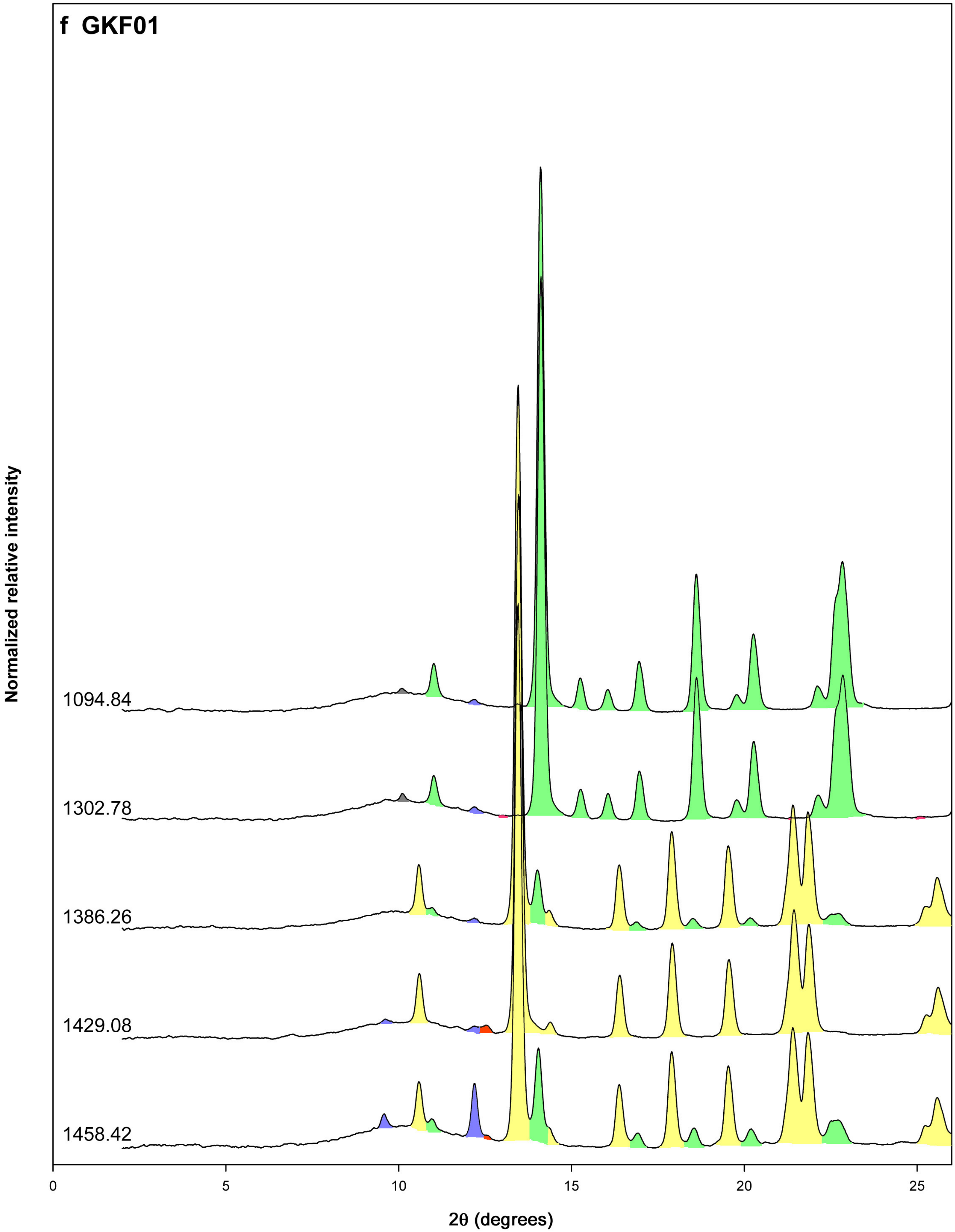


c GKP01 (continued)
Normalized relative intensity
619.00
634.45
667.00
693.84
755.51
796.22
0
5
10
15
20
25
2θ (degrees)


d GKP01 (continued)
Normalized relative intensity
859.90
911.80
987.27
1198.45
1207.34
1211.70
0
5
10
15
20
25
2θ (degrees)



e GKF01
Normalized relative intensity
331.90
395.40
570.16
745.12
790.18
925.90
0
5
10
15
20
25
2θ (degrees)



f GKF01
Normalized relative intensity
1094.84
1302.78
1386.26
1429.08
1458.42
0
5
10
15
20
25
2θ (degrees)

Figure EA-1-2. XRD patterns for samples analyzed here for Fe isotope composition (**a–d**, core GKP01; **e–f**, core GKF01). The intensity of all spectra were normalized to the tallest peak in each spectrum: GKP01 315.60–987.27 and GKF01 331.90–1302.78, [1 0 4] of dolomite/ankerite; GKP01 1198.45 and GKF01 1386.26–1458.42, [1 0 4] of calcite; and GKP01 1207.34–1211.70, [1 0 1] of quartz. Patterns were acquired from 2θ angles of 2 to 44°, but shown here are the patterns from 2 to 26º, a range that includes the vast majority of peaks of interest for carbonates, Fe oxides, pyrite, and silicates. No baseline subtraction was performed.

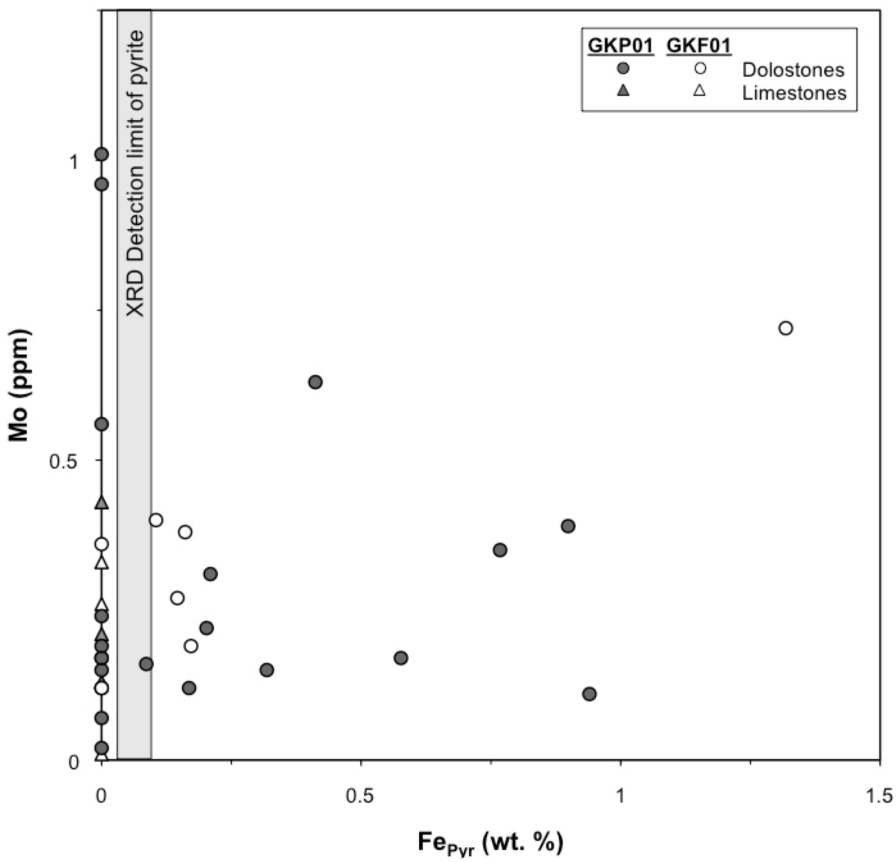


Figure EA-1-3. Whole-rock carbonate Mo content versus Fe content in pyrite for carbonates from cores GKP01 (gray symbols) and GKF01 (open symbols). The experimentally determined detection limit for pyrite by our XRD methods is ~0.10 wt.% (~0.05 wt.% for pyrite Fe).

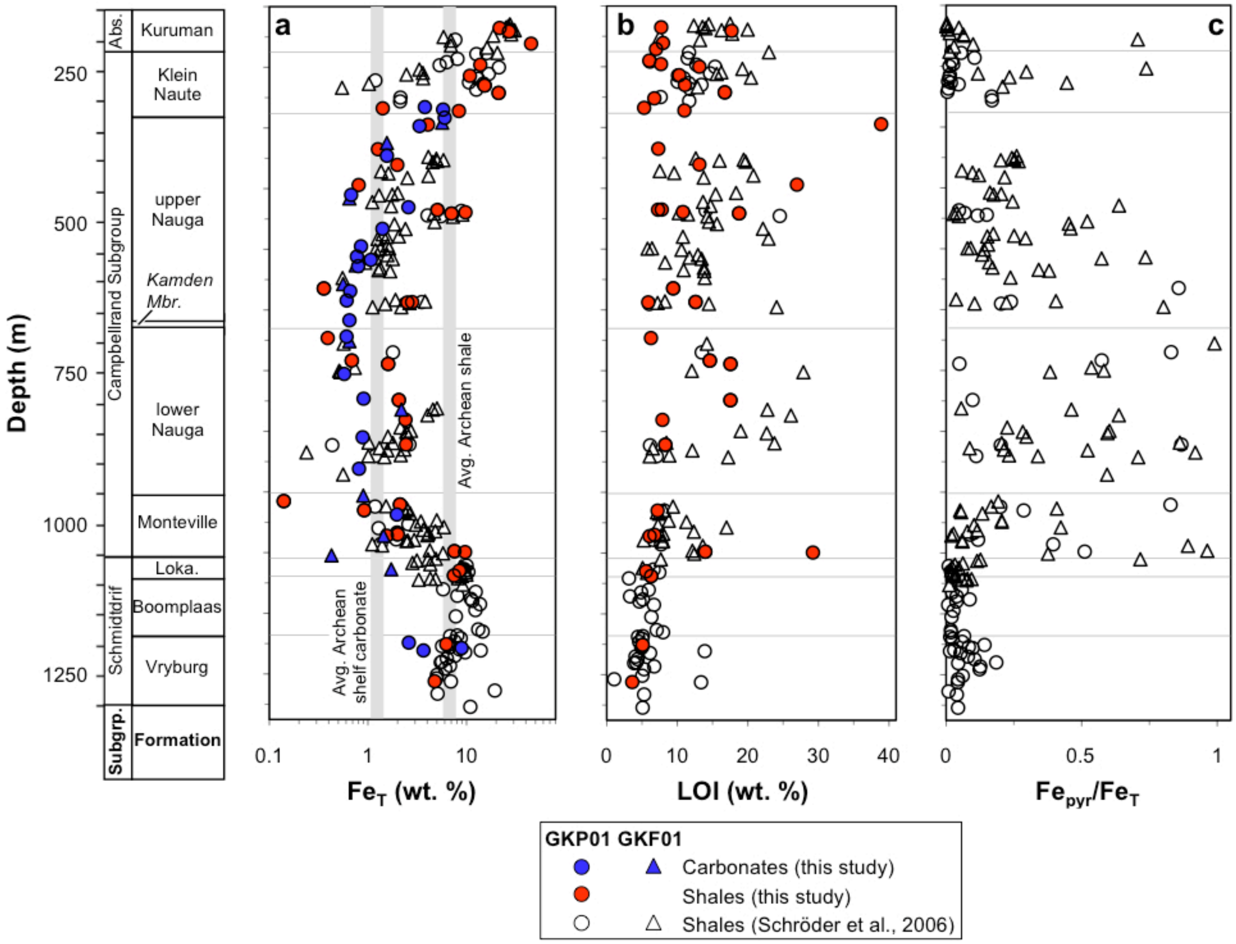


Figure EA-1-4. Whole-rock geochemical data for carbonates and shales from cores GKP01 and GKF01 from the Neoarchean–Paleoproterozoic Campbellrand–Malmani platform of South Africa. Blue symbols represent carbonates from this study (Table EA-2-2), red symbols represent shales from this study (Table EA-2-3), and open symbols represent shale data reported by Schröder et al. (2006). Total Fe contents (Fe_T) (**a**) indicate that the samples from the Monteville and Nauga formations are generally Fe poor relative to the average of Archean shales (Fe_T = 6.72 wt.%; Taylor and McLennan, 1985) and plot closer to the average of Archean shelf carbonates (Fe_T = 1.24 wt.%; Veizer et al., 1990). Comparison of the shale data with masses lost on ignition (LOI) (**b**), which include carbonate CO_3, suggests that many of these shale samples are relatively carbonate-rich. Many of the carbonate- rich samples from these cores also have a high proportion of pyrite Fe in their total Fe budgets (**c**). Pyrite Fe (Fe_{pyr}) was calculated from published S data (Schröder et al., 2006) assuming a stoichiometry of FeS_2 for pyrite.

Supplemental references

Schröder S., Lacassie J. P. and Beukes N. J. (2006) Stratigraphic and geochemical framework of the Agouron drill cores, Transvaal Supergroup (Neoarchean-Paleoproterozoic, South Africa). *S. Afr. J. Geol.* 109, 23-54.

Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: its Composition and Evolution.* Blackwell Scientific Publications, Oxford.

Veizer J., Clayton R. N., Hinton R. W., von Brunn V., Mason T. R., Buck S. G. and Hoefs J. (1990) Geochemistry of Precambrian carbonates: 3-shelf seas and non-marine environments of the Archean. *Geochim. Cosmochim. Acta* 54, 2717-2729.