Supporting information:

Solid state NMR of salivary calculi: proline-rich salivary proteins, citrate, polysaccharide, lipid, and organic-mineral interactions.

Yang Li[a], David G. Reid[a], Dominique Bazin[b,c], Michel Daudon[d], Melinda J. Duer[a]

[a] Department of Chemistry, University of Cambridge, Lensfield Rd., Cambridge CB2 1EW, UK.
[b] Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, 91405 Orsay, France.
[c] Laboratoire de Chimie de la Matière Condensée de Paris UniversitéPierre et Marie Curie et Collège de France, 11 place Marcelin Berthelot, 75231 Paris cedex 05, France.
[d] APHP, Hôpital Tenon, Service d' Explorations Fonctionnelles, 4 rue de la Chine, 75020 Paris, France.

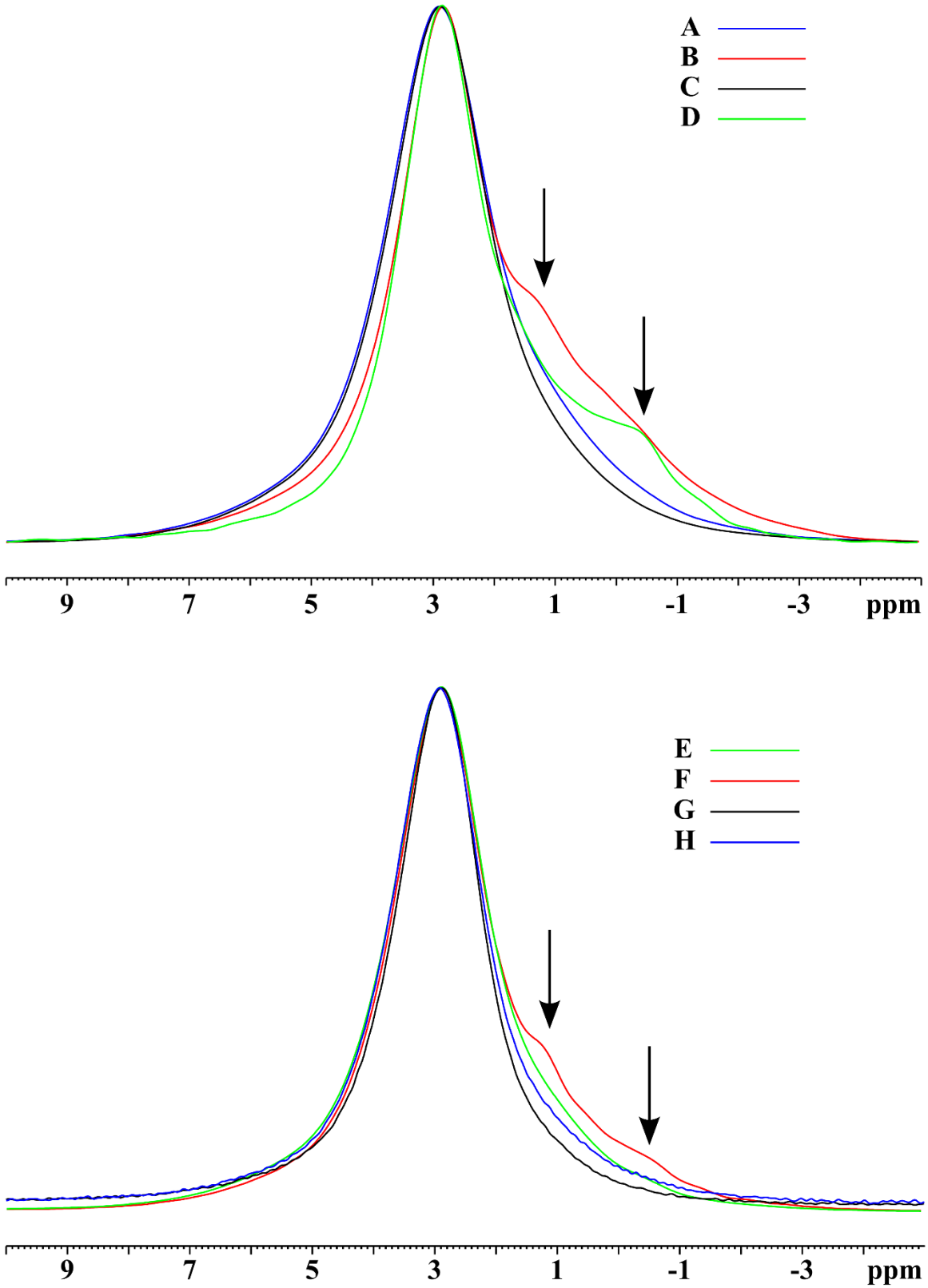

Fig. S1 Overlays of the ^{31}P spectra of all eight stones. Arrows denote the shoulders discussed in the text.

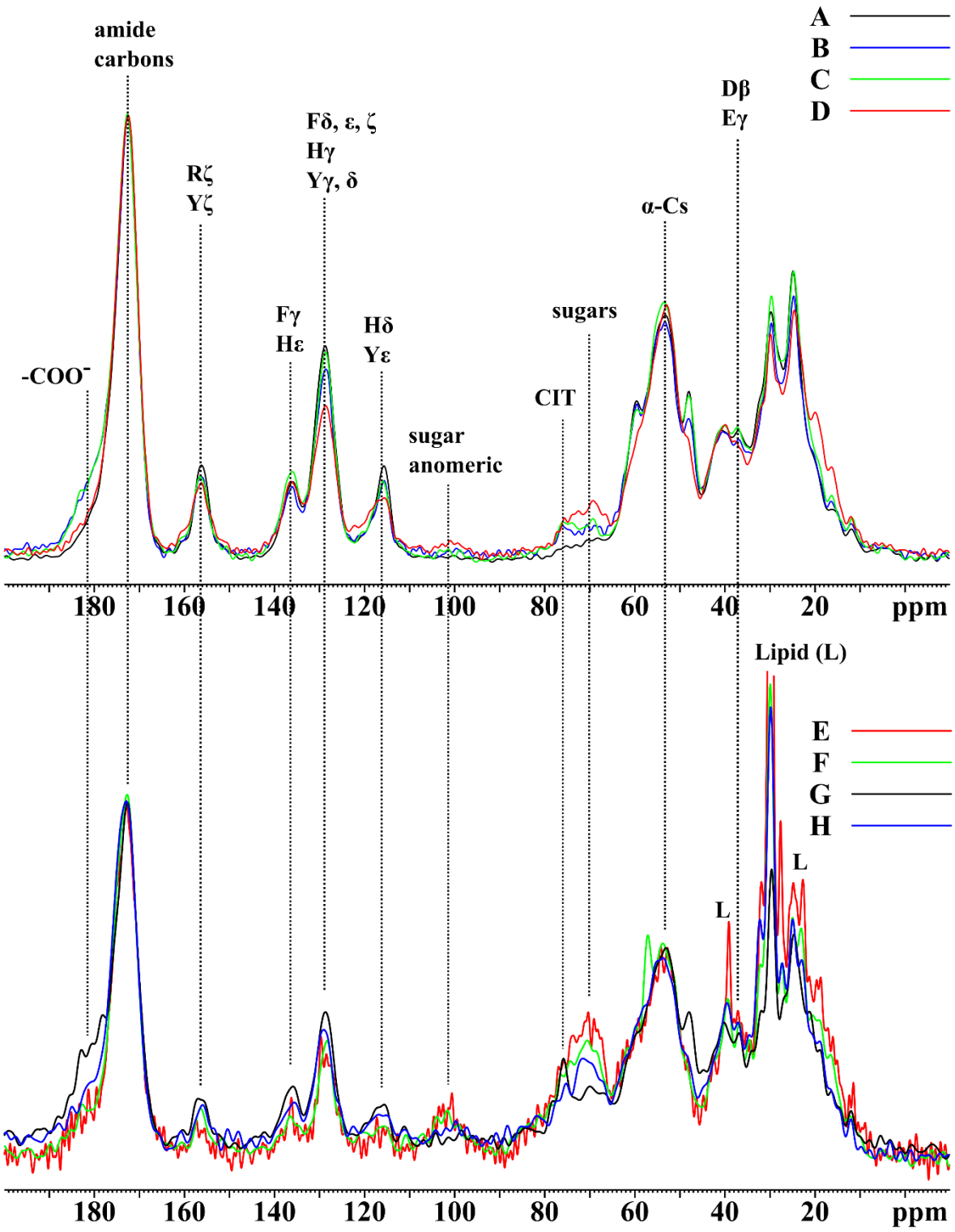

Fig. S2 Overlays of the ^{13}C spectra of all eight stones.

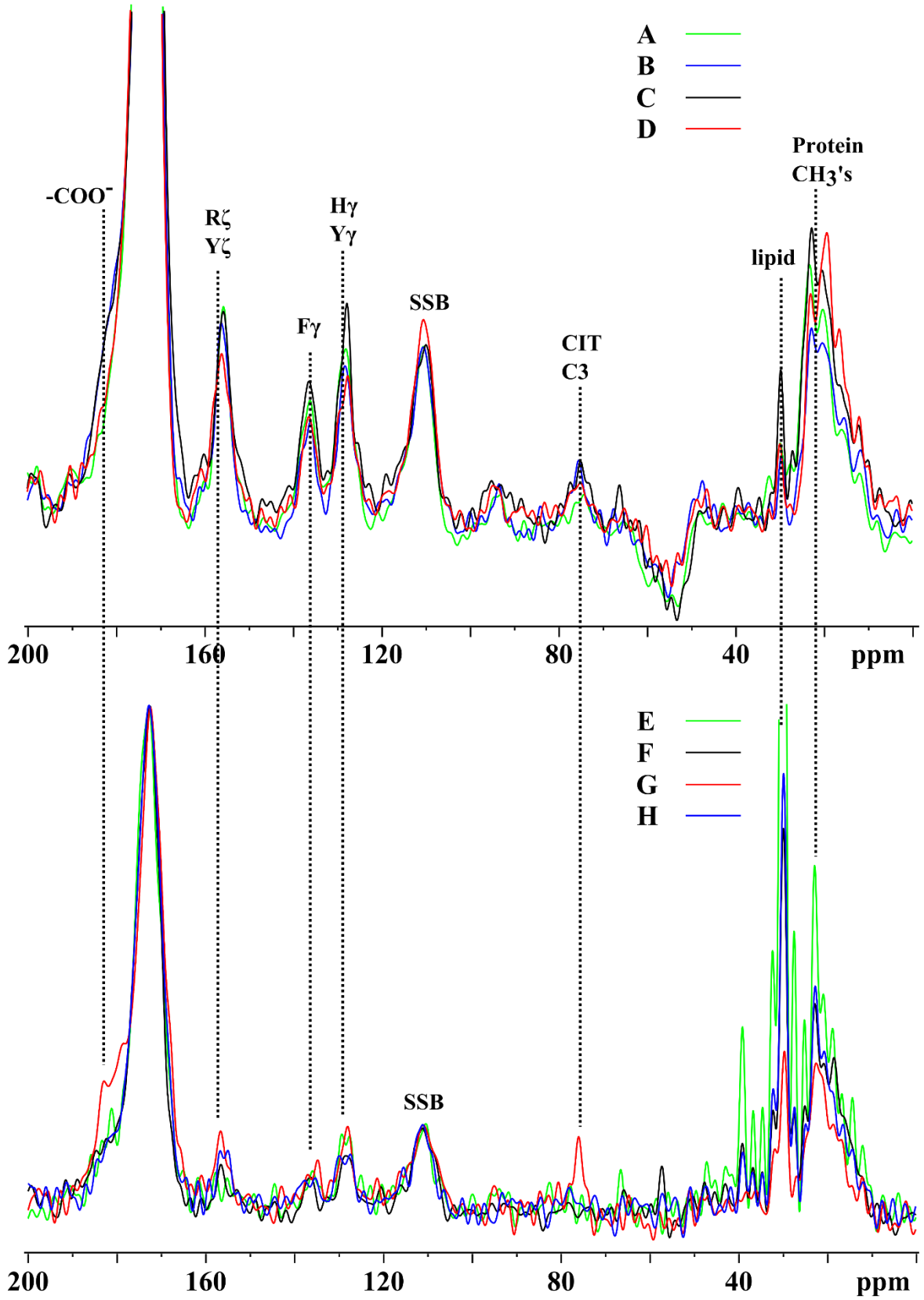

Fig. S3 Overlays of the dipolar dephased (DD) spectra of all eight stones. SSSB – spinning side band.

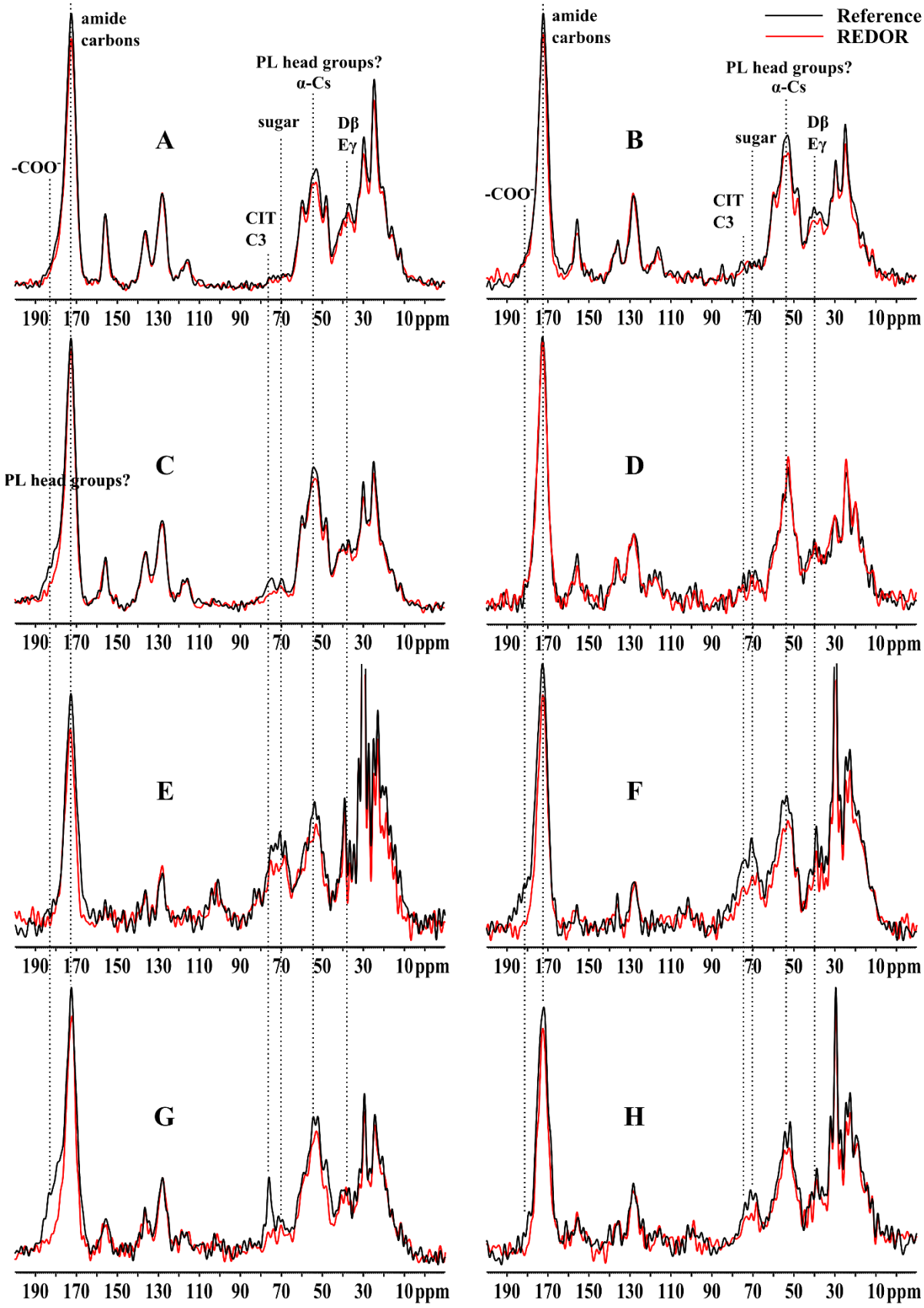

Fig. S4 Overlays of the $^{13}C\{^{31}P\}$ REDOR datasets of all eight stones.

Table S1 Measured amino acid composition from each of two analyses per sample of the four stones analysed; meaned data for each stone appears in Table 1.

Amino acid	Sample / Mole %							
	A		B		C		D	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Ala	2.6	2.9	2.1	3.7	3.5	3.8	5.0	5.1
Arg	7.7	7.8	7.8	7.6	8.2	8.1	7.0	7.0
Asp	5.4	5.5	4.5	5.7	6.1	6.1	9.4	9.3
Glu	15.5	14.8	16.3	14.5	14.1	14.1	10.7	10.5
Gly	9.8	9.8	9.5	9.1	9.6	9.5	10.5	10.3
His	5.9	6.0	4.9	4.3	7.5	7.3	8.4	8.5
Ile	3.3	3.4	3.2	4.4	3.4	3.5	3.3	3.4
Leu	5.2	5.3	5.0	6.2	4.9	5.1	6.6	6.6
Lys	4.0	4.1	3.8	4.1	4.9	5.0	6.0	6.0
Met	0.6	0.5	0.5	0.8	0.7	0.6	1.4	1.4
Phe	7.6	7.6	7.7	7.4	8.3	8.4	5.8	5.9
Pro	13.3	13.3	15.6	13.5	11.8	11.8	5.7	5.8
Ser	3.0	3.0	2.5	2.8	2.6	2.6	4.1	4.1
Thr	2.1	2.2	1.8	2.3	1.7	1.8	3.7	3.6
Tyr	10.7	10.4	11.6	9.6	9.5	8.8	6.7	6.6
Val	3.5	3.6	3.2	4.1	3.4	3.4	5.9	6.0

Notes summarizing compositional data (by FT-IR), and NMR results

A Carbapatite (50%)+proteins (35%)+whitlockite (15%)

NMR ^{31}P: No low frequency shoulders. ^{13}C: Small broad sugar signal. Small ^{13}C{^{31}P} REDOR to 35 – 40 ppm and 50 – 60 ppm signal envelopes, and amides. Lipid not prominent.

B Carbapatite (65%)+proteins (25%)+whitlockite (10%)

NMR ^{31}P: Prominent shoulder ca. 1.3 and 0 ppm. ^{13}C: Small citrate and sugar signals. ^{13}C{^{31}P} REDOR to 35 – 40 ppm and 50 – 60 ppm signal envelopes, and amides. Lipid not prominent

C Carbapatite (77%)+proteins (20%)+triglycerides (3%)

NMR ^{31}P: No shoulders on HAp peak. ^{13}C: Lipid not prominent; Citrate and sugar undergo ^{13}C{^{31}P} REDOR as well as 50 – 60 ppm signal envelope, amides, and carboxylate.

D Carbapatite (55%)+whitlockite (25%)+proteins (20%)

NMR ^{31}P: Shoulder -0.5 – 0 ppm. ^{13}C: Poor S/N, little ^{13}C{^{31}P} REDOR, or lipid signal.

E: Salivary stone from a male patient aged 27 years living in Tahiti. Stone morphology: unusual. Stone composition: Carbapatite (72%), Hydroxyapatite (10%)+Proteins (15%)+Lipids (probably triglycerides and/or esters of cholesterol and fatty acids) (3%).

NMR ^{31}P: No shoulders on HAp peak ^{13}C: Lipid very prominent. ^{13}C{^{31}P} REDOR to sugars, 50 – 60 ppm signal envelope, amides, and possibly to lipid.

F: Salivary stone from a male patient aged 18 years. Stone morphology: IVa+VIb. Stone composition: Carbapatite (80%), Proteins (20%).

NMR ^{31}P: Shoulders at 1.1 ppm, -0.5 ppm ^{13}C: ^{13}C{^{31}P} REDOR to citrate and sugars, and 50 – 60 ppm signal envelope, amides, and carboxylates. Lipid present.

G Salivary stone from a male patient aged 72 years: Stone morphology: IVa+VIb. Stone composition: Carbapatite (72%)+Hydroxyapatite (15%)+Proteins (13%).

NMR ^{31}P: No shoulders on HAp peak ^{13}C: Prominent citrate which undergoes strong ^{13}C{^{31}P} REDOR, also ^{13}C{^{31}P} REDOR to 35 – 40 ppm and 50 – 60 ppm signal envelopes, amides, and carboxylate.

H Salivary stone from a male patient. Stone morphology: IVa+VIb. Stone composition: Carbapatite (88%)+Proteins (12%).

NMR ^{31}P: No shoulders on HAp peak. ^{13}C: Poor S/N but citrate and sugar undergo ^{13}C{^{31}P} REDOR as well as 50 – 60 ppm signal envelope, amides, and carboxylate. Some lipid.