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NMR SPECTROSCOPY OF EXPERIMENTALLY SHOCKED SILICATE MINERALS*

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ABSTRACT

Magic-angle spinning nuclear magnetic resonance (MAS NMR) techniques were used to analyze experimentally shocked quartz and feldspar powders. ^{29}Si NMR spectra were determined for quartz and labradorite feldspar and ^{27}Al and ^{23}Na spectra for labradorite. Both minerals were shocked to 7.5, 16.5, and 22 GPa using the Sandia "Momma Bear" recovery fixtures. The MAS NMR results for quartz are in full agreement with previous measurements, indicating a high degree of reproducibility. Numerical decomposition of quartz data are consistent with two distinct phases: a defective crystalline quartz and an amorphous-like silica phase. There is a strong correlation between the fraction of amorphous phase and the mean peak shock pressure. The labradorite data are much more complicated, consisting of multiple peaks with no obvious correlation with shock pressure. No amorphous phase was evident from the NMR spectra of the shocked labradorite, nor were high pressure phases detectable for either mineral.

INTRODUCTION

Recent studies[1,2] have determined that solid state nuclear magnetic resonance (NMR) spectroscopy is extremely sensitive to the disorder brought about by shock-loading of quartz. The technique has distinct advantages for the identification of shocked quartz in bulk samples, as compared to X-ray, electron microscopy, optical, or density methods.

We have performed additional shock-loading experiments and NMR analysis of quartz and feldspar powders in an effort to 1) determine the reproducibility of previous results, 2) further characterize the NMR spectra with spectral deconvolution techniques, 3) provide additional basis for use of the NMR technique as an empirical shock barometer, and 4) determine whether more complicated silicate minerals, such as plagioclase feldspars, exhibit similar trends.

EXPERIMENTAL METHOD

Shock recovery experiments reported previously[2] were repeated by shocking synthetic quartz samples at two different initial densities (corresponding to two different shock temperatures at each pressure) to mean peak pressures of 7.5,16.5, and 22 GPa using the Sandia "Momma Bear" explosive loading fixtures.[3,4] Table 1 provides a summary of the conditions of the shock recovery experiments for these samples.

The only substantive difference between these and previous experiments is the manner in which the quartz was prepared prior to the shock-loading experiments. The identical synthetic quartz powder was used, however it was annealed at 900°C for 20 hours to minimize the initial defect densities which had previously broadened the (101) X-ray diffraction peak. Unshocked and annealed samples were subjected to extensive characterization by optical, X-ray, and NMR techniques. The effect of annealing on the peak widths (full width at half maximum) of NMR spectra was negligible compared to the broadening observed after shock-loading.

A natural labradorite feldspar ($Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$) from Pueblo Park, New Mexico was prepared in a similar fashion. The starting material was annealed at 900°C for 20 hours prior to shock-loading. A summary of the labradorite shock experiments is also provided in Table 1.

The NMR experiment measures the radio frequency emission from specific NMR-active nuclei (for example, ^{29}Si, ^{27}Al, and ^{23}Na) which have been excited to a higher energy state while the sample is located in a very strong magnetic field. NMR analysis required magic-angle

spinning (MAS) and multi-pulse Fourier transform techniques to provide spectra with significantly decreased interference from dipolar interactions and improved signal to noise ratio.[2,5]

RESULTS AND DISCUSSION

Examples of the ^{29}Si MAS NMR spectra for the unshocked and shocked quartz powders are provided in Figure 1. Resonance frequencies are presented in terms of chemical shift (ppm relative to an external standard). Split Pearson VII curve fits[6] were used to provide a numerical determination of the spectral characteristics including the peak width. The spectrum of the 22 GPa (high shock temperature) quartz sample exhibits substantial peak broadening as a result of the shock-loading.

Figure 2 provides a comparison of the relative changes in ^{29}Si NMR peak width as a function of shock pressure for each temperature set. Values from the earlier experiments on quartz[2] were fully reproduced with peak width measurements in agreement within the reported error bars.

Decomposition of the measured NMR spectra into two Lorentzian peaks was carried out by way of a six parameter fitting routine (two intensities, two widths, and two positions). The resulting function provides a good fit to the data in all cases for shocked quartz. In Figure 3, the raw data are shown with the two-peak solution for the 22 GPa high shock temperature quartz experiment. The two component peaks can be associated with two distinct phases of SiO_2; the narrow peak corresponding to a defective crystalline quartz phase and the broad peak belonging to an amorphous or highly disordered phase.

Further evidence for this association comes from reduction of the broad peak after partial dissolution of the recovered powder in hydrofluoric acid (see Figure 3), implying that the amorphous material

is selectively dissolved, as expected. Relative peak width values for the 16.5 and 22 GPa high shock temperature samples after being subjected to acid etching are also plotted in Figure 2. Despite the relatively large amplitude of the NMR signal associated with amorphous silica, there is no X-ray diffraction or optical evidence for glass in the shocked samples. Preliminary analysis of NMR relaxation times for the shocked samples suggests that the broadening of the NMR peak can be attributed to amorphous material that is less than 1 weight percent.

The identification of two distinct phases in the NMR spectra provides a strong basis for using NMR spectroscopy of quartz as a shock barometer. The broadening of the overall NMR peak systematically increases as a function of shock pressure, and the deconvolution demonstrates this broadening is due primarily to the increasing contribution of the amorphous component.

In addition to the NMR analysis of the shocked quartz powders, we obtained NMR spectra for the annealed and shocked labradorite samples. NMR spectra were determined for ^{29}Si, ^{27}Al, and ^{23}Na nuclei. Because of the large number of silicon sites in the tetrahedral framework of this feldspar, and the higher spin of the ^{27}Al and ^{23}Na nuclei, the spectra are complicated (consisting of six to eight multiple peaks for ^{29}Si) and are difficult to interpret. There is no evidence from the NMR data, or from optical and X-ray examination, for the formation of an amorphous phase in labradorite as a result of the shock-loading.

CONCLUSIONS

MAS NMR spectroscopy of quartz powders is extremely sensitive to disorder produced by shock-loading. Analysis of the spectra provides evidence of crystalline disorder and the formation of an amorphous-like phase. The level of disorder increases with shock pressure so as to increasingly broaden the ^{29}Si resonance. This broadening can be used as a shock barometer for controlled shock-loading of well-characterized quartz powders. The NMR spectra of the labradorite powders did not exhibit any feature that strongly correlates with shock pressure.

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TABLE 1 Schedule of shock recovery experiments

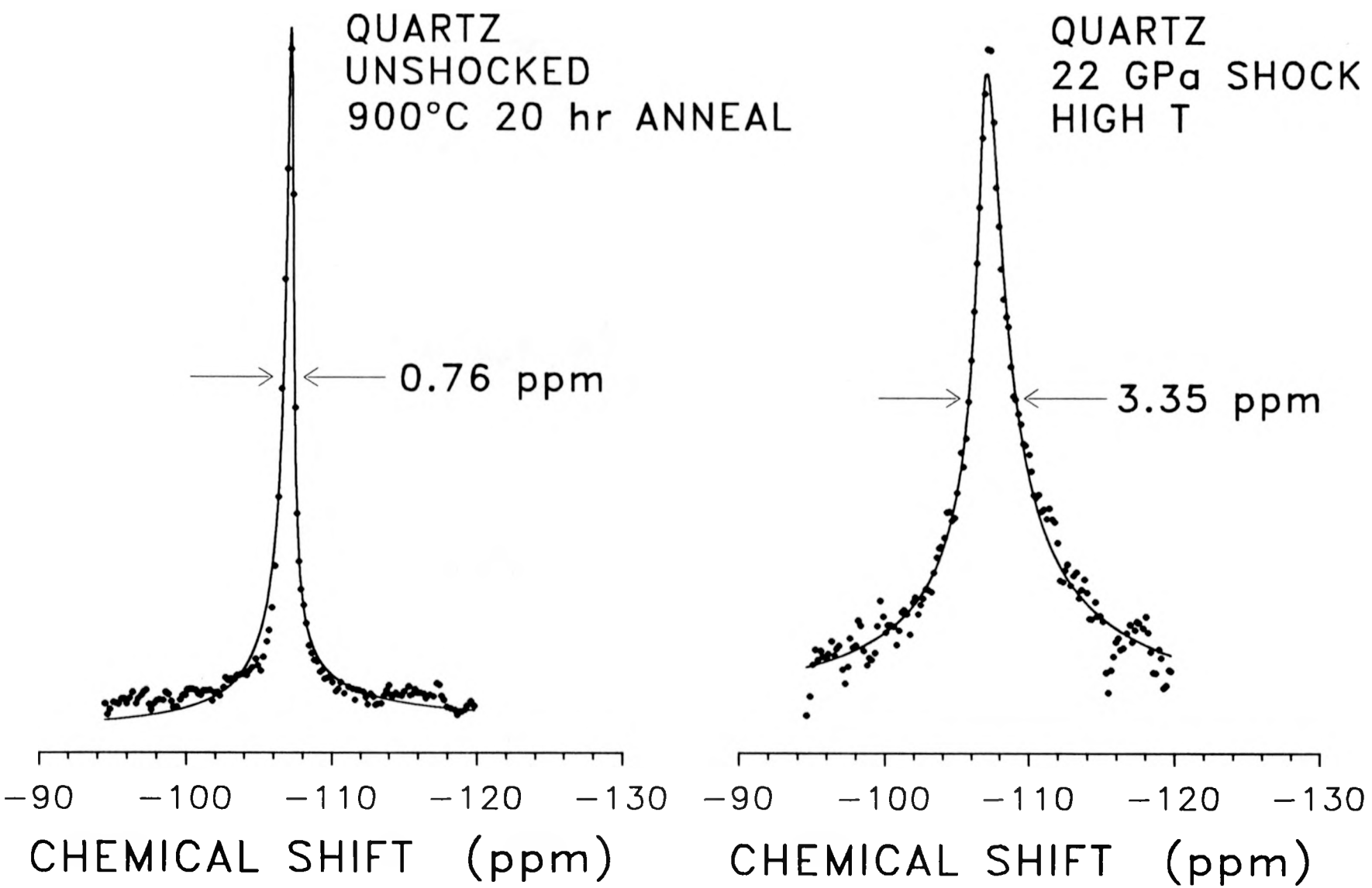
SHOT	MATERIAL	FIXTURE/ EXPLOSIVE	SAMPLE COMPACT DENSITY (%)	MEAN PEAK PRESSURE (GPa)	ESTIMATED MEAN BULK TEMPERATURE (°C)
8B906	quartz	Momma/Baratol	60.5	7.5	150-175
5B906	quartz	Momma/Comp B	60.4	16.5	325-475
2B906	quartz	Momma-A/Comp B	60.3	22	325-575
9B906	quartz	Momma/Baratol	51.4	7.5	300-325
6B906	quartz	Momma/Comp B	51.2	16.5	475-600
3B906	quartz	Momma-A/Comp B	51.3	22	450-700
7B906	labradorite	Momma/Baratol	48.1	7.5	325-350
4B906	labradorite	Momma/Comp B	48.0	16.5	500-625
1B906	labradorite	Momma-A/Comp B	48.0	22	500-725

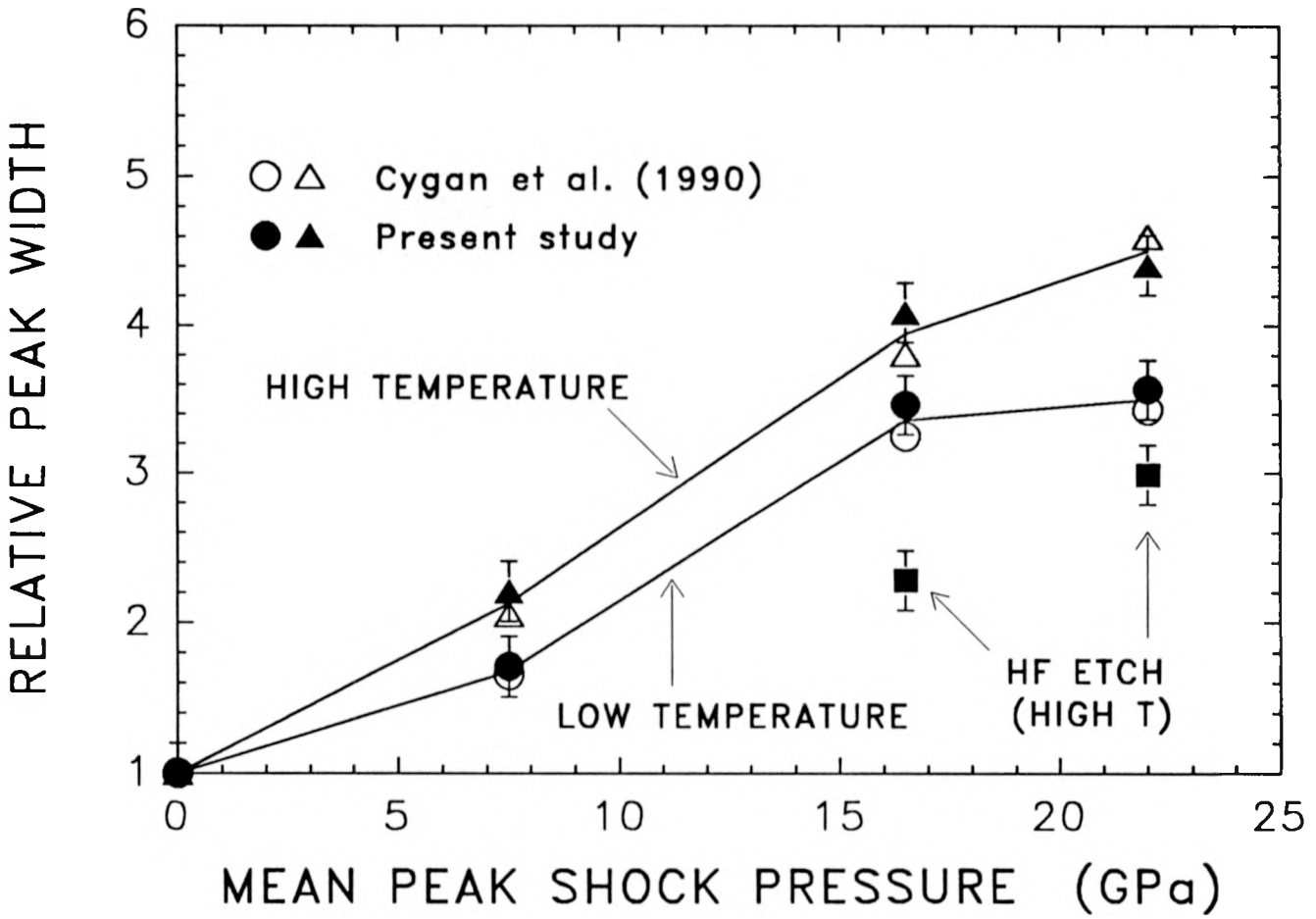
FIGURE CAPTIONS

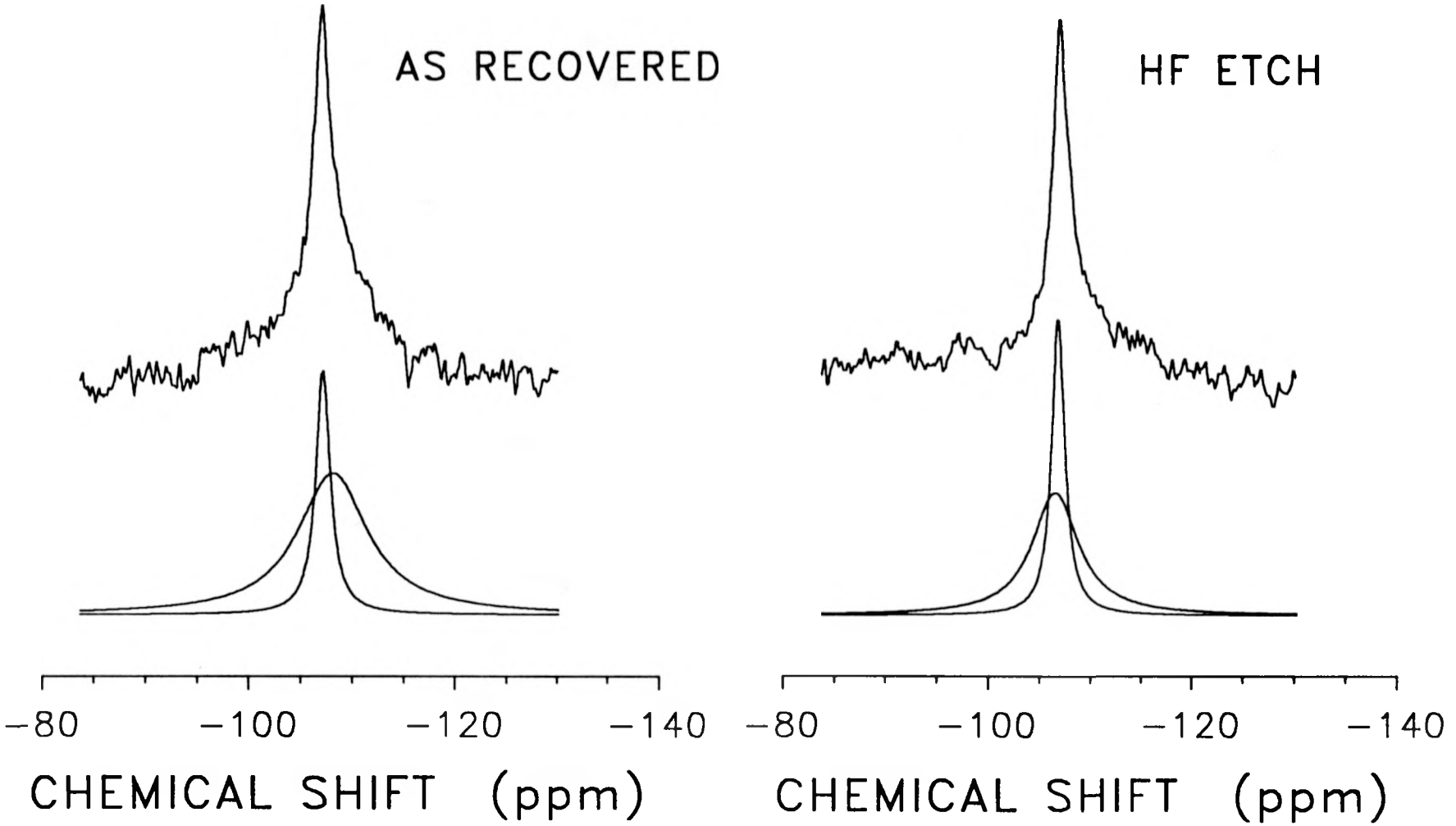
Figure 1. Comparison of ^{29}Si MAS NMR spectra and split Pearson VII fits for the unshocked and 22 GPa (high shock temperature) quartz samples.

Figure 2. Comparison of relative changes in NMR peak widths for powdered quartz samples as a function of shock pressure. Error bars are shown only for the data from the present study.

Figure 3. Deconvolutions of ^{29}Si MAS NMR spectra for the 22 GPa high temperature quartz sample as recovered and after HF acid treatment.


QUARTZ
UNSHOCKED
900°C 20 hr ANNEAL
0.76 ppm
−90
−100
−110
−120
−130
CHEMICAL SHIFT (ppm)
QUARTZ
22 GPa SHOCK
HIGH T
3.35 ppm
−90
−100
−110
−120
−130
CHEMICAL SHIFT (ppm)


RELATIVE PEAK WIDTH
MEAN PEAK SHOCK PRESSURE (GPa)
Cygan et al. (1990)
Present study
HIGH TEMPERATURE
LOW TEMPERATURE
HF ETCH
(HIGH T)
1
2
3
4
5
6
0
5
10
15
20
25


AS RECOVERED
HF ETCH
−80
−100
−120
−140
CHEMICAL SHIFT (ppm)
−80
−100
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−140
CHEMICAL SHIFT (ppm)