Data Mining with the PDF-4 Databases

FeO Non-stoichiometric Oxides

This is one of three example-based tutorials for using the data mining capabilities of the PDF-4+ database and it covers the following topic:

- **FeO Non-stoichiometric Oxides**
  - sorting out temperature and stoichiometric effects on cell parameters

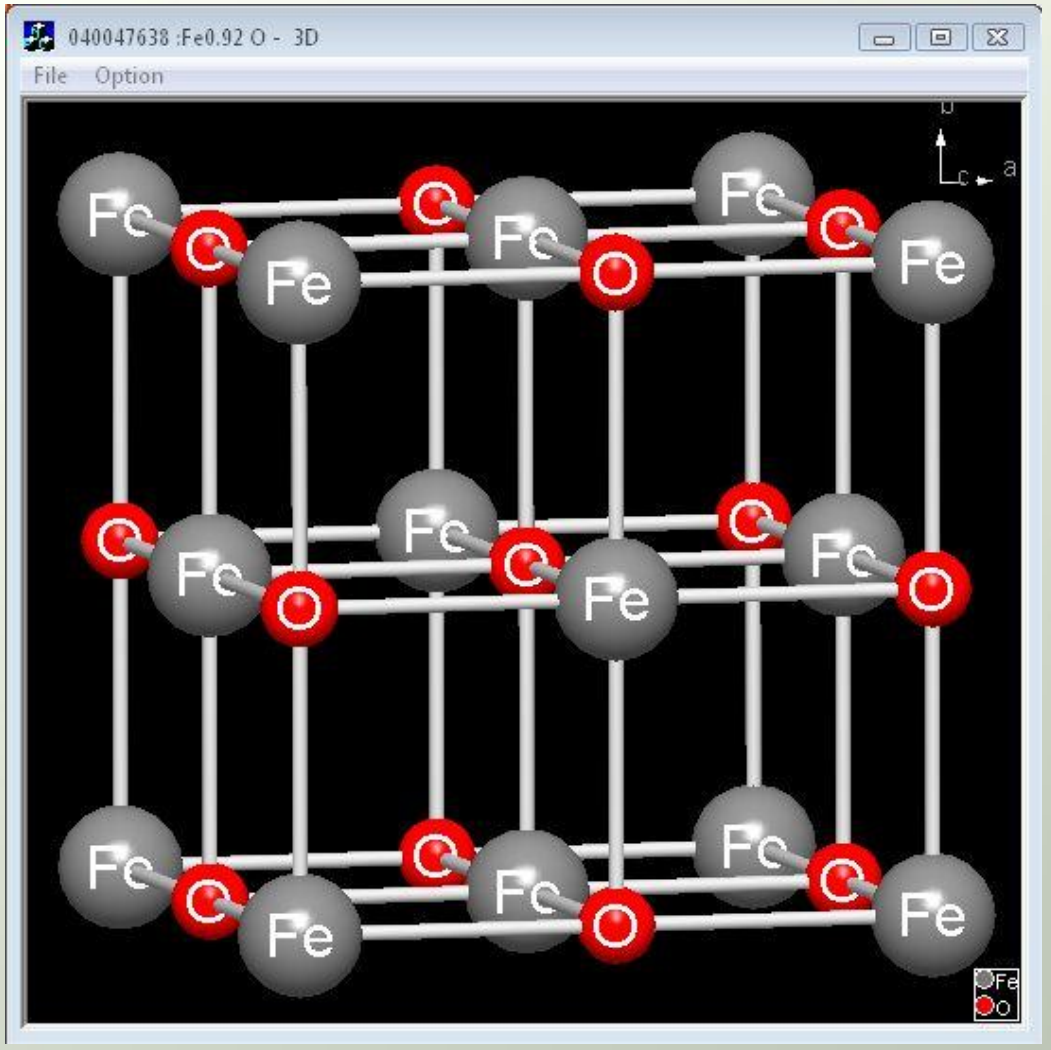
Two other similar tutorials for data mining exist and cover the following topics:

- **CIGS Photovoltaics (Solid Solution Example)**
  - solid solution / cell parameter relationship
- **Carbamazepine (Resolving Pharmaceutical Polymorphs)**
  - a PDF-4/Organics application
  - investigating polymorphic forms of an active pharmaceutical ingredient (API)

Stoichiometric Factors Affecting the Diffraction Pattern of FeO

- FeO is frequently non-stoichiometric with Fe-site vacancies.
- These defects have crystallographic effects and can cause shifts in the observed powder diffraction peaks.
- Summaries of this effect can be “mined” from the PDF-4+ database and displayed for further study.

Crystal Structure of FeO*



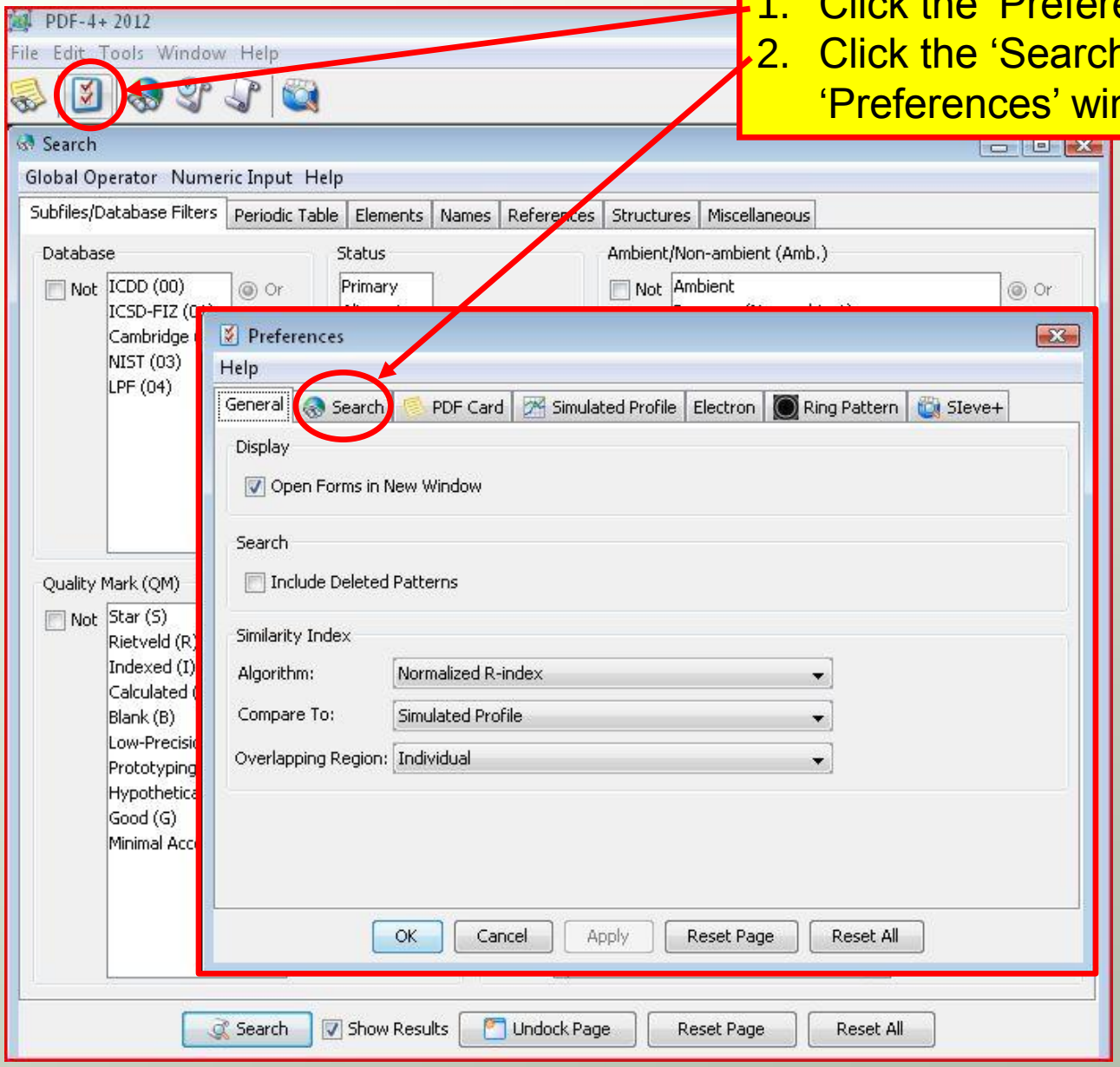
Cubic System
Space Group: Fm-3m
NaCl type structure

*Structure taken from PDF entry 04-004-7638 calculated from the Linus Pauling File database (MPDS).

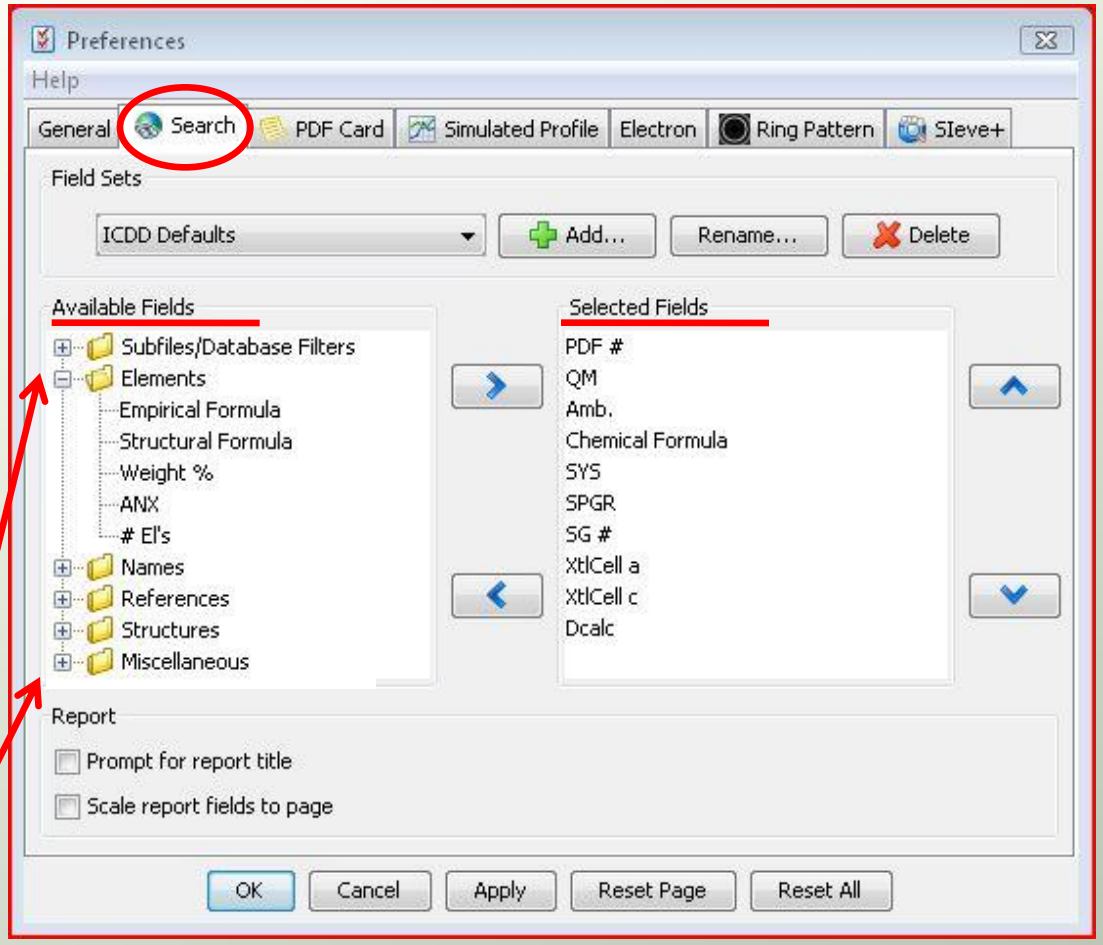
Data Mining for FeO Entries: Step 1

Use the Preferences Window to establish what will be displayed in the Search Results table . . .

1. Click the 'Preferences' icon
2. Click the 'Search' tab in the 'Preferences' window

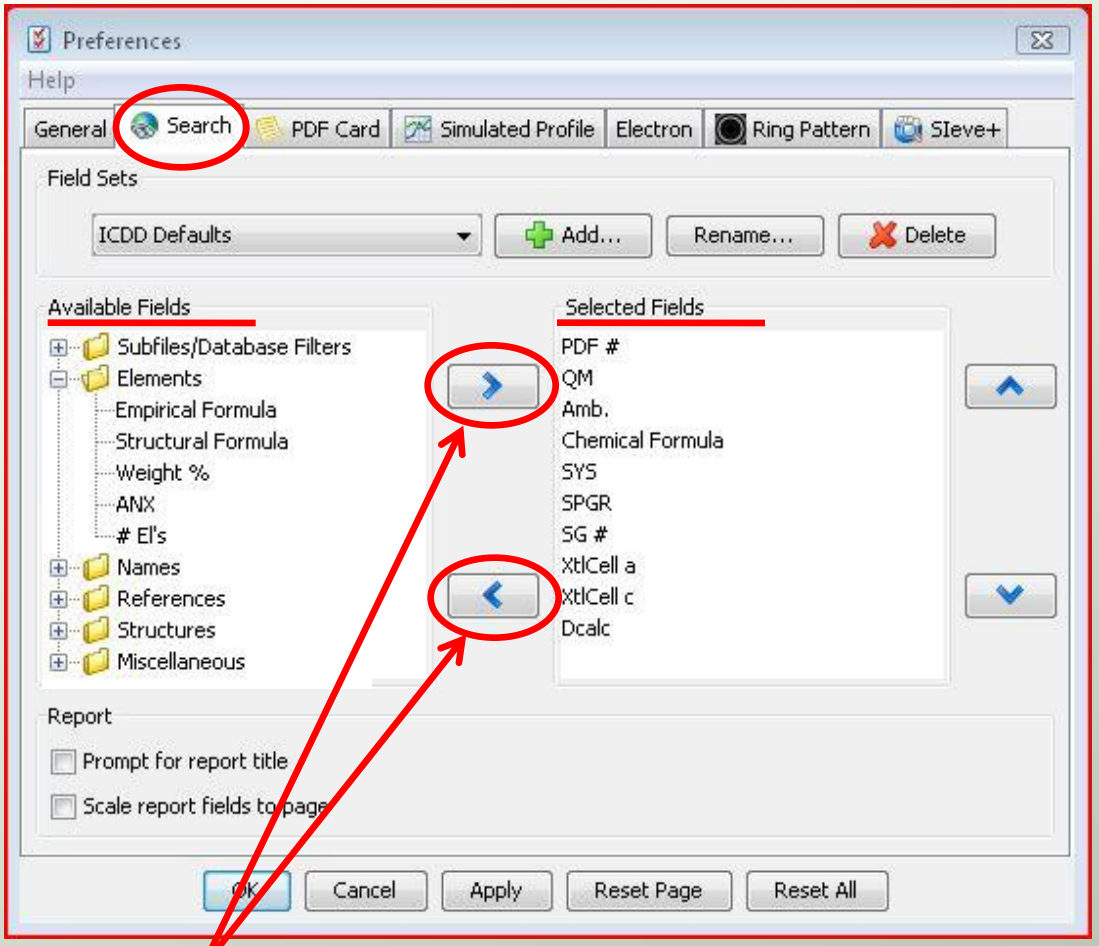


Selecting Fields for the Results Table



Expandable folders contain individual fields

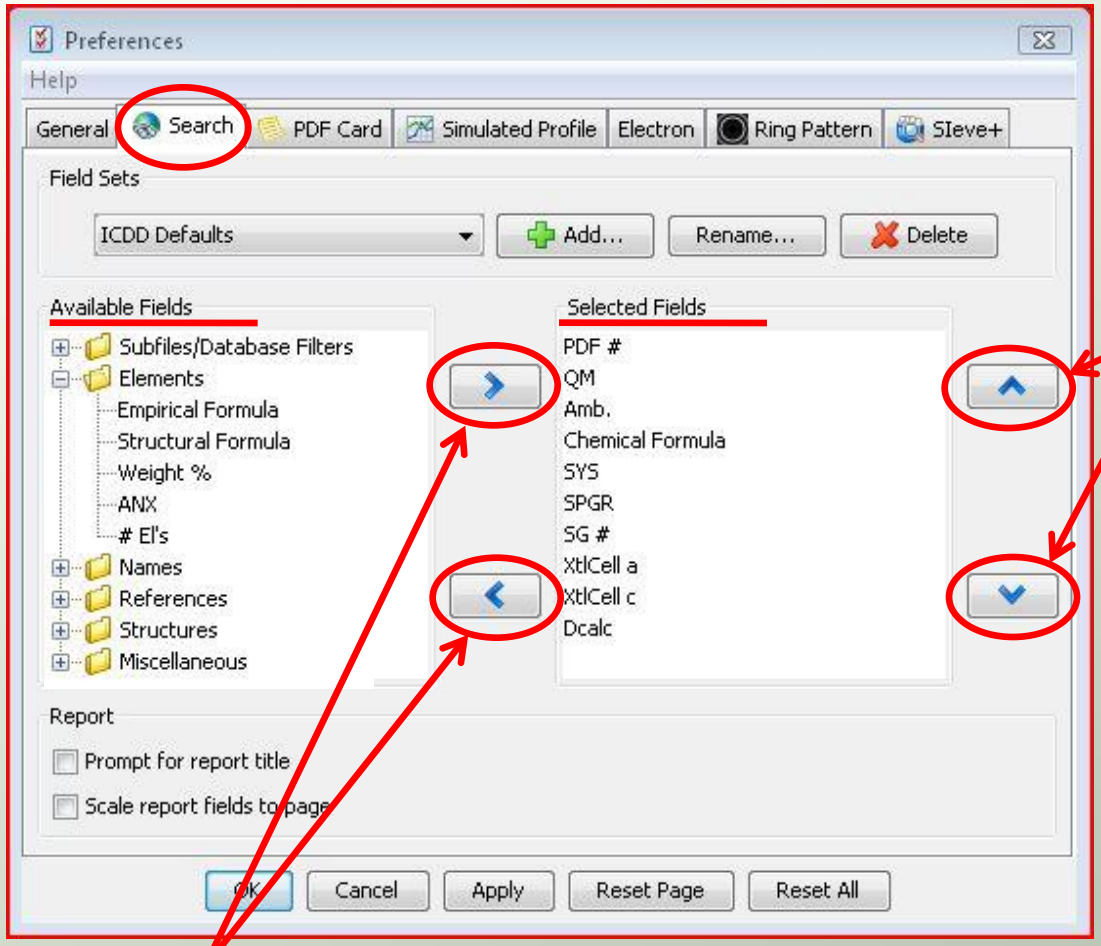
Selecting Fields for the Results Table



Available Fields:

Use these buttons to move selected items between the 'Available Fields' list of 90 items and the 'Selected Fields' list of items that will be displayed in the results table.

Selecting Fields for the Results Table



Selected Fields:

Use these buttons to move a selected item up or down in the listed order for the results table.

Available Fields:

Use these buttons to move selected items between the 'Available Fields' list of 90 items and the 'Selected Fields' list of items that will be displayed in the results table.

Selecting Fields for Results Table (FeO)

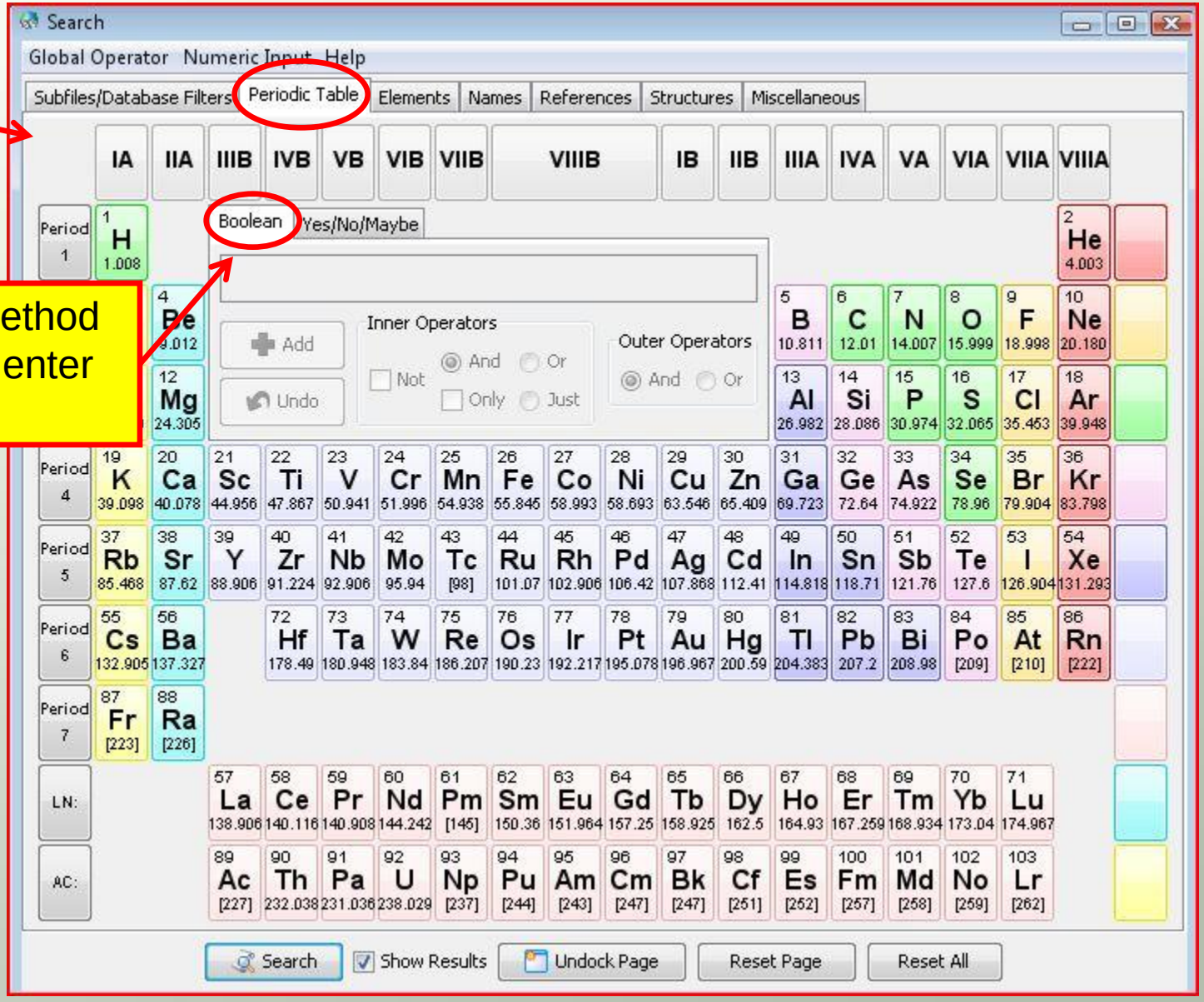
Selected Fields		Available Fields folder
PDF #	-	Always selected
QM	-	Subfiles/Database Filters
Amb.	-	Subfiles/Database Filters
Chemical Formula		Elements
Atomic %	-	Elements
SYS	-	Structures
SPGR	-	Structures
SG #	-	Structures
XtlCell-a	-	Structures
Dcalc	-	Miscellaneous

Setting up the fields as shown here will serve the purposes of this example. (Click 'OK' at the bottom of the 'Preferences' screen when finished.)

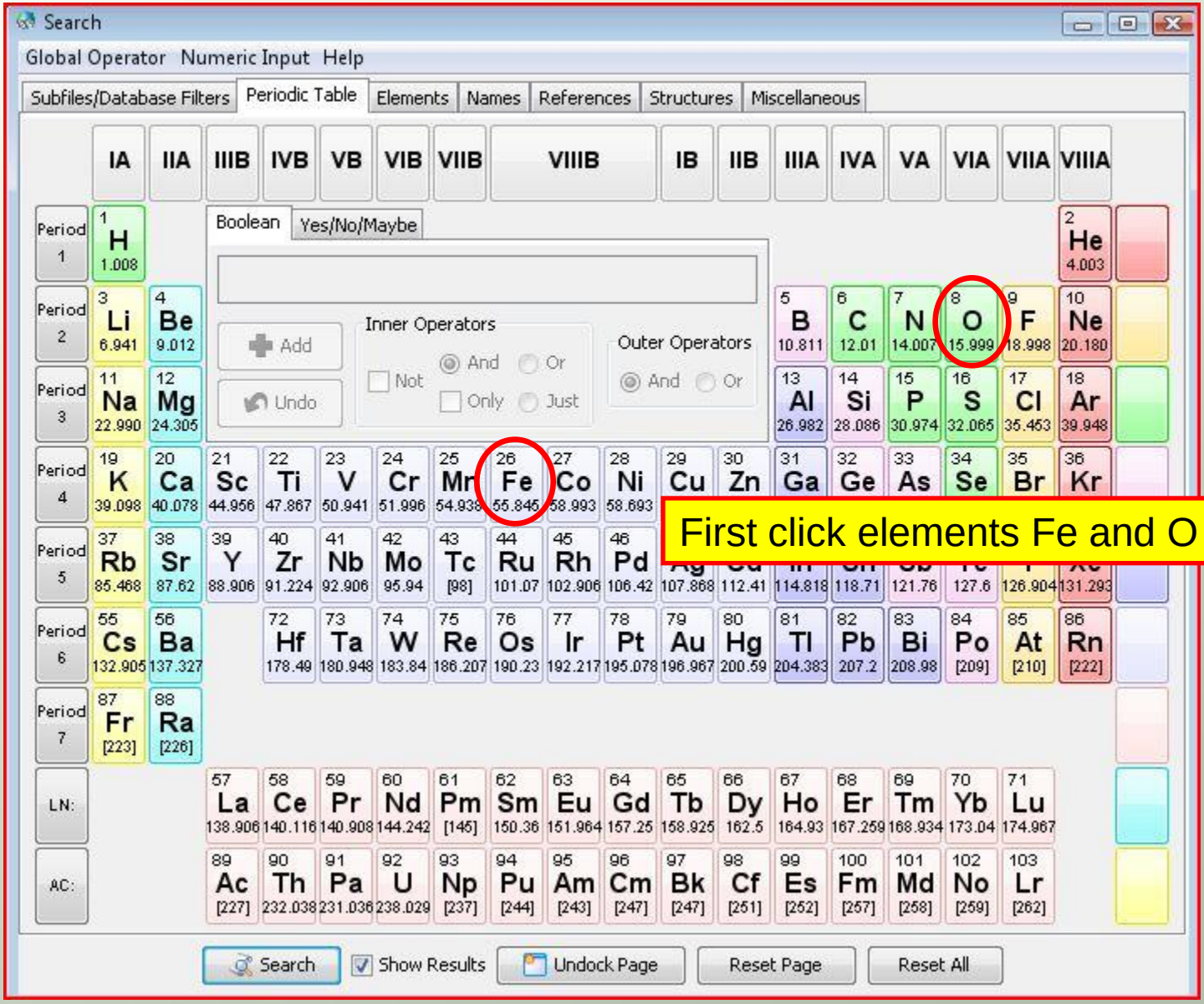
Chemistry Criterion for Search: **Fe and O only** entered on 'Periodic Table' tab of 'Search' window

Search Window Icon

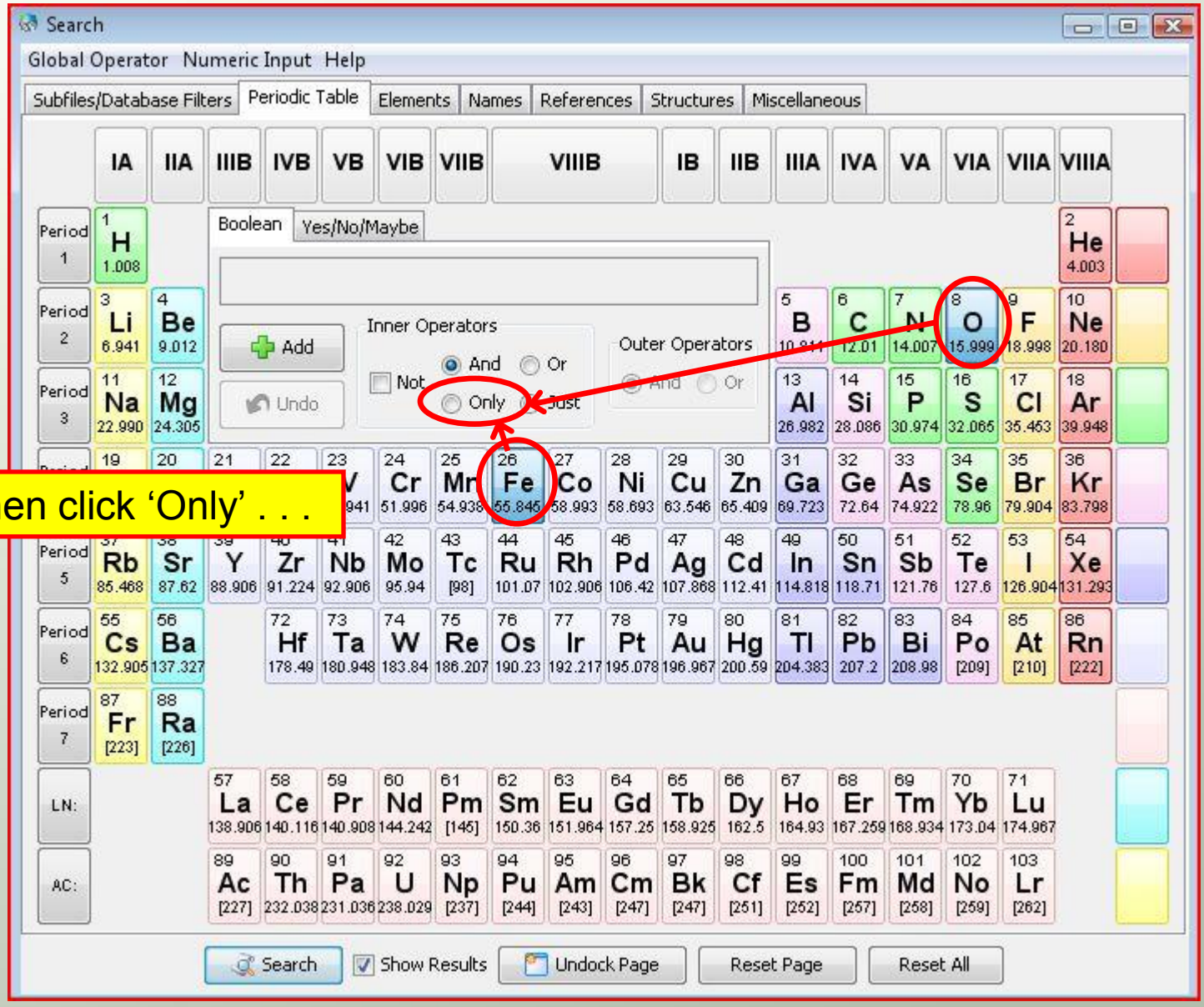
The Boolean method can be used to enter this criterion.



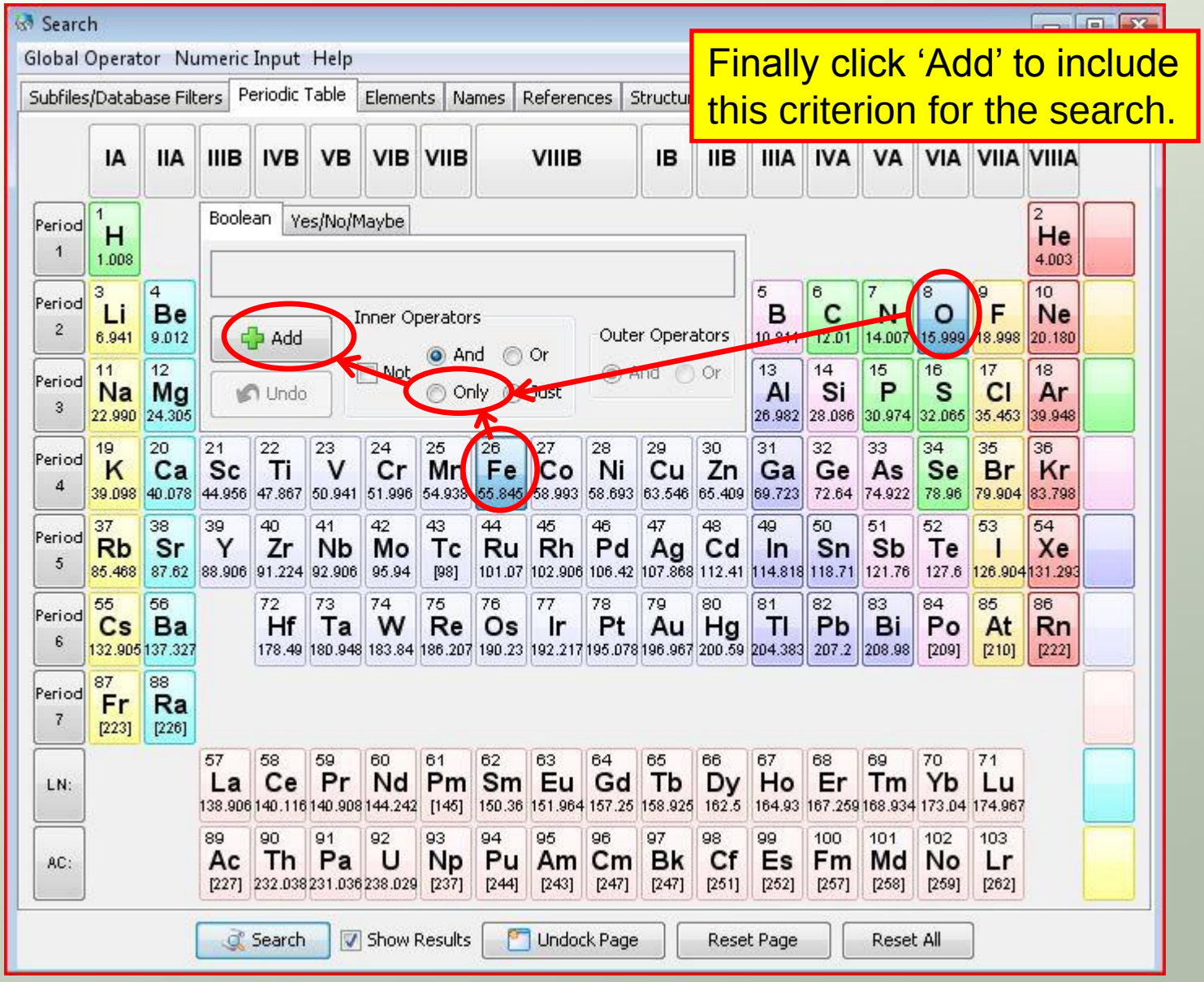
Chemistry Criterion for Search: **Fe and O only** entered on 'Periodic Table' tab of 'Search' window



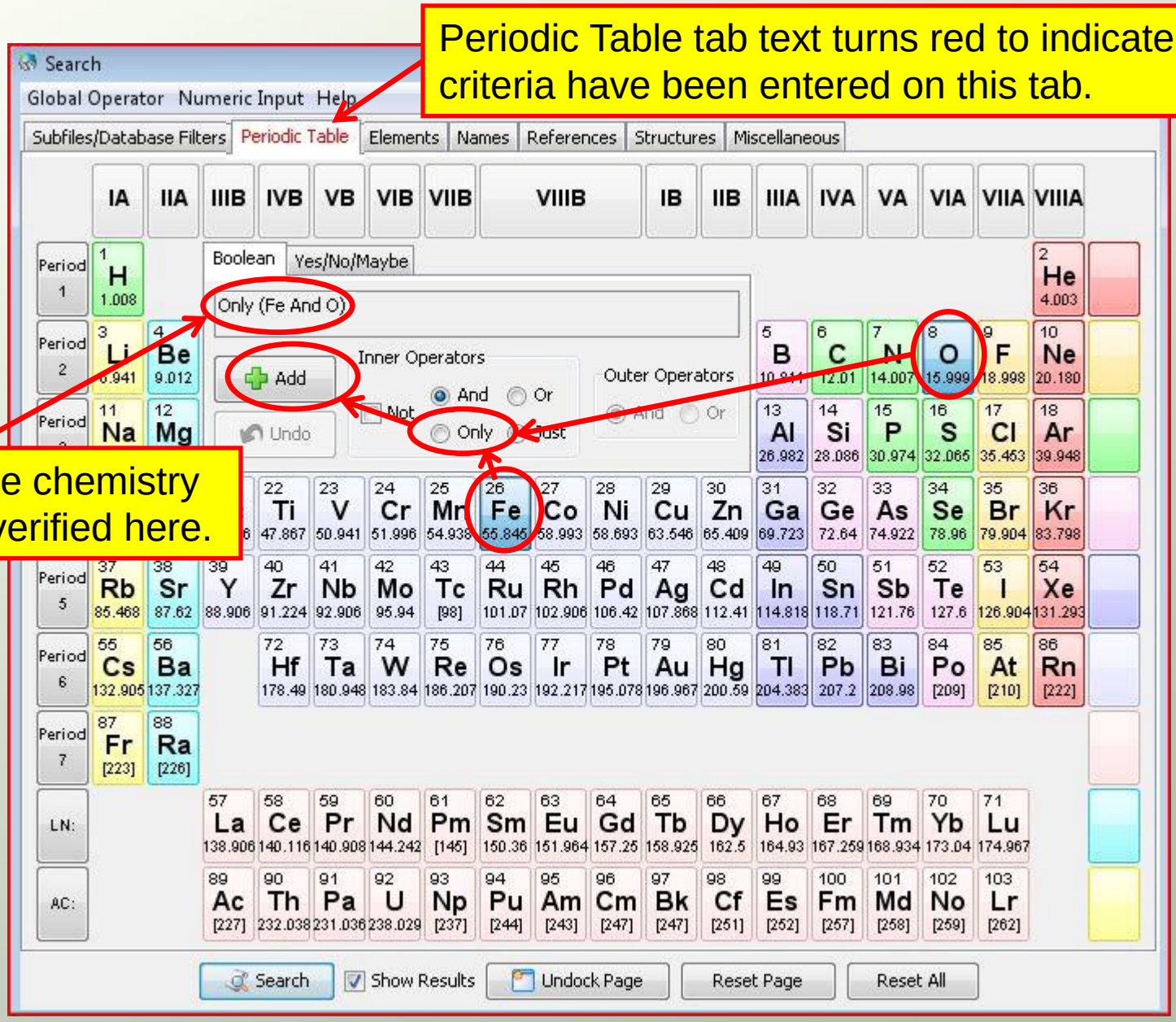
Chemistry Criterion for Search: **Fe and O only** entered on 'Periodic Table' tab of 'Search' window



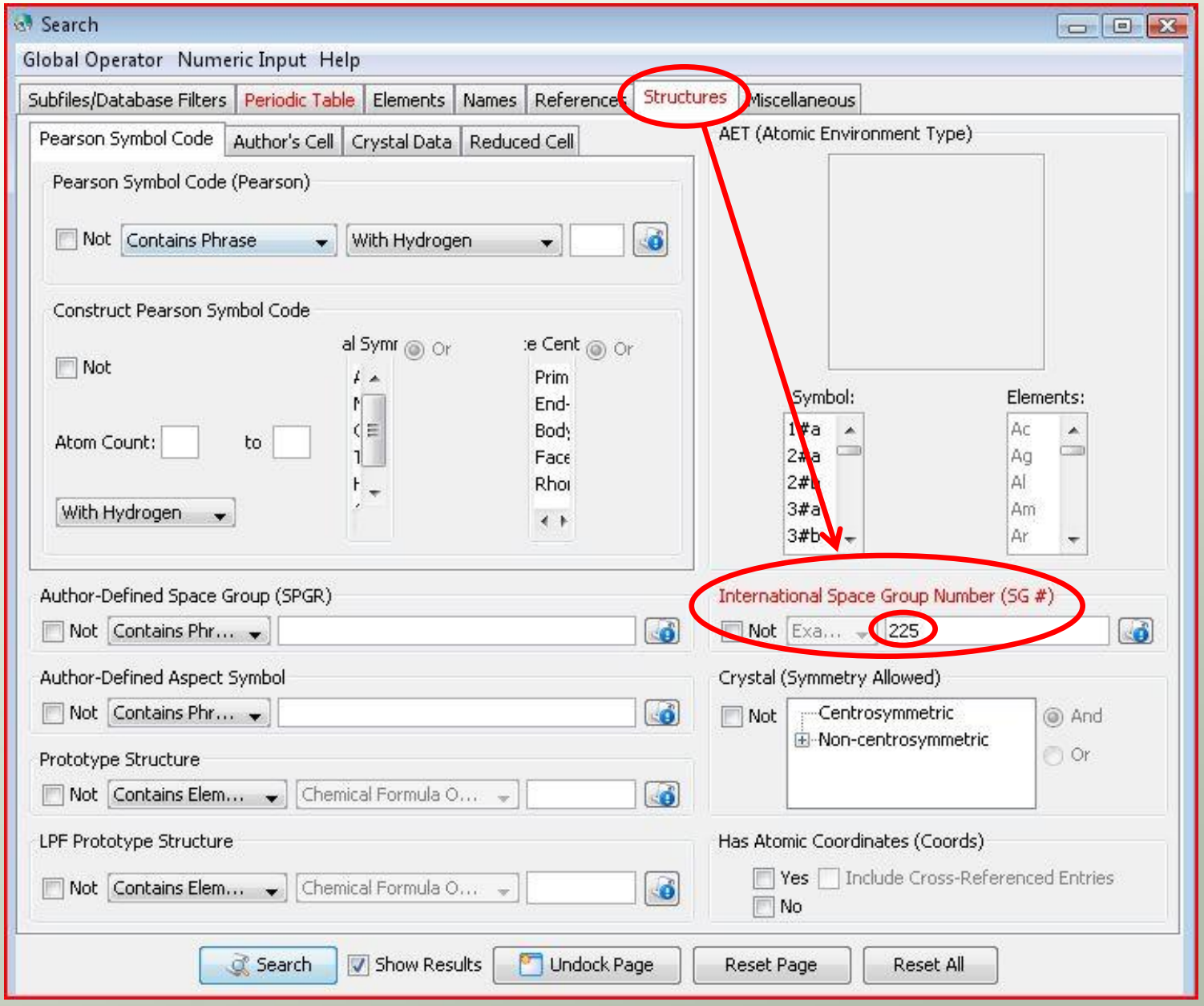
Chemistry Criterion for Search: **Fe and O only** entered on 'Periodic Table' tab of 'Search' window



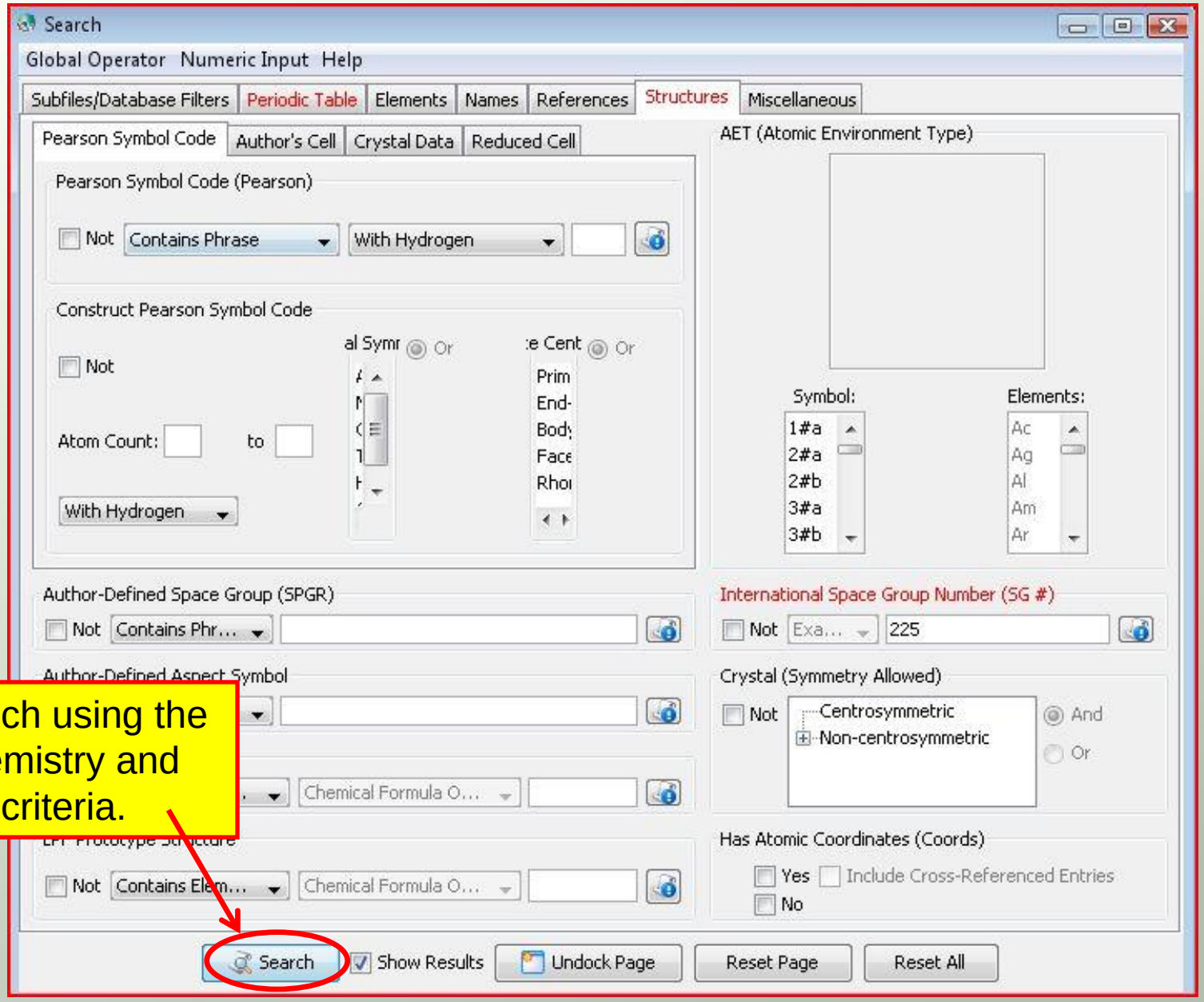
Chemistry Criterion for Search: **Fe and O only** entered on 'Periodic Table' tab of 'Search' window



Structure Criterion for Search: **FCC Space Group #225 – 'Fm-3m'** entered on 'Structures' tab of 'Search' window



Structure Criterion for Search: **FCC Space Group #225 – 'Fm-3m'** entered on 'Structures' tab of 'Search' window



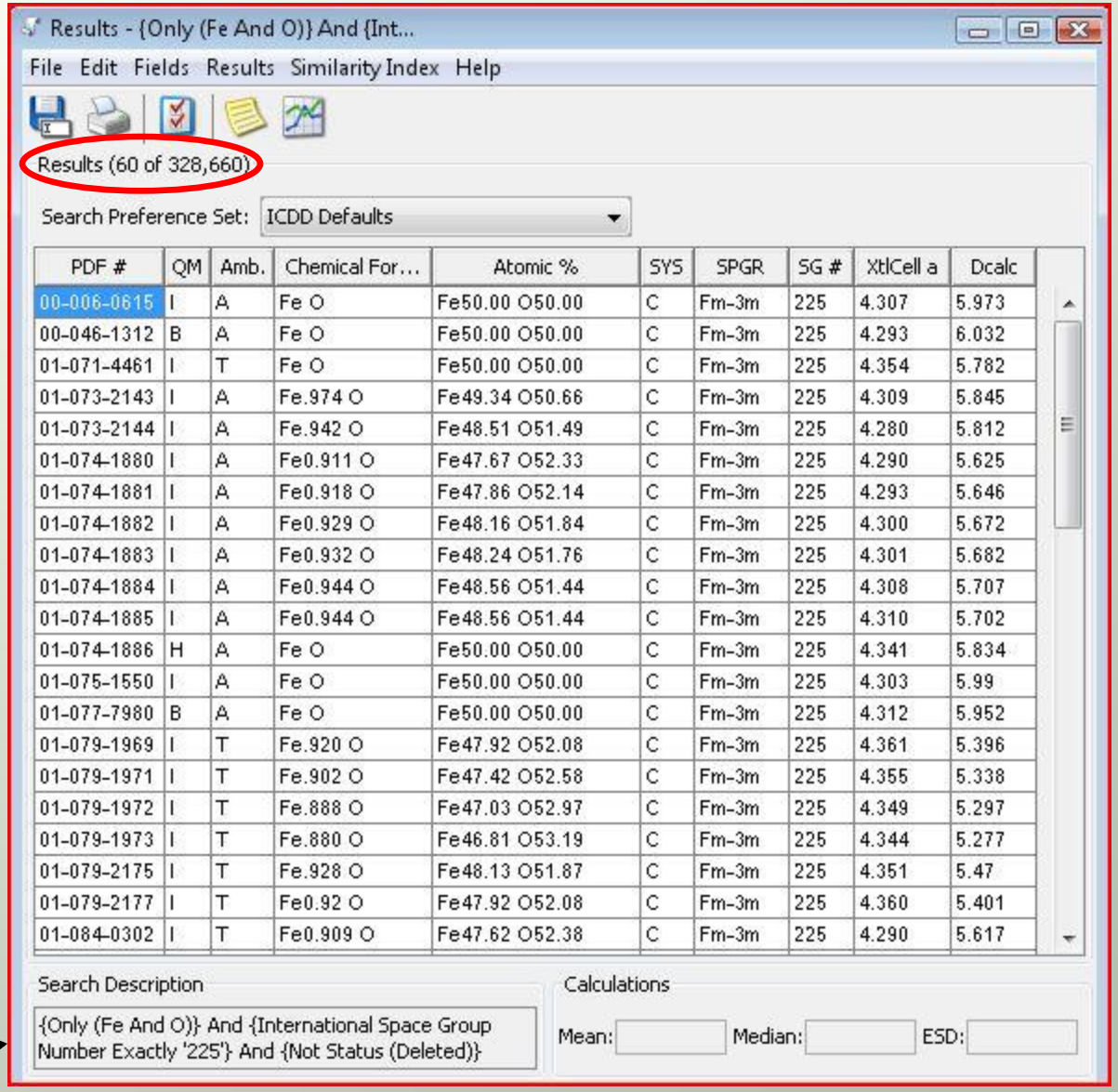
Perform search using the specified chemistry and space group criteria.

Results of PDF-4+ Search for FeO

A total of 60 entries for $Fe_{1-x}O$ compounds

You will get 66 entries if the 'Include Deleted Patterns' box is checked on the 'Subfiles/ Database Filters' tab of the Search window.

A description of your search criteria is shown here.



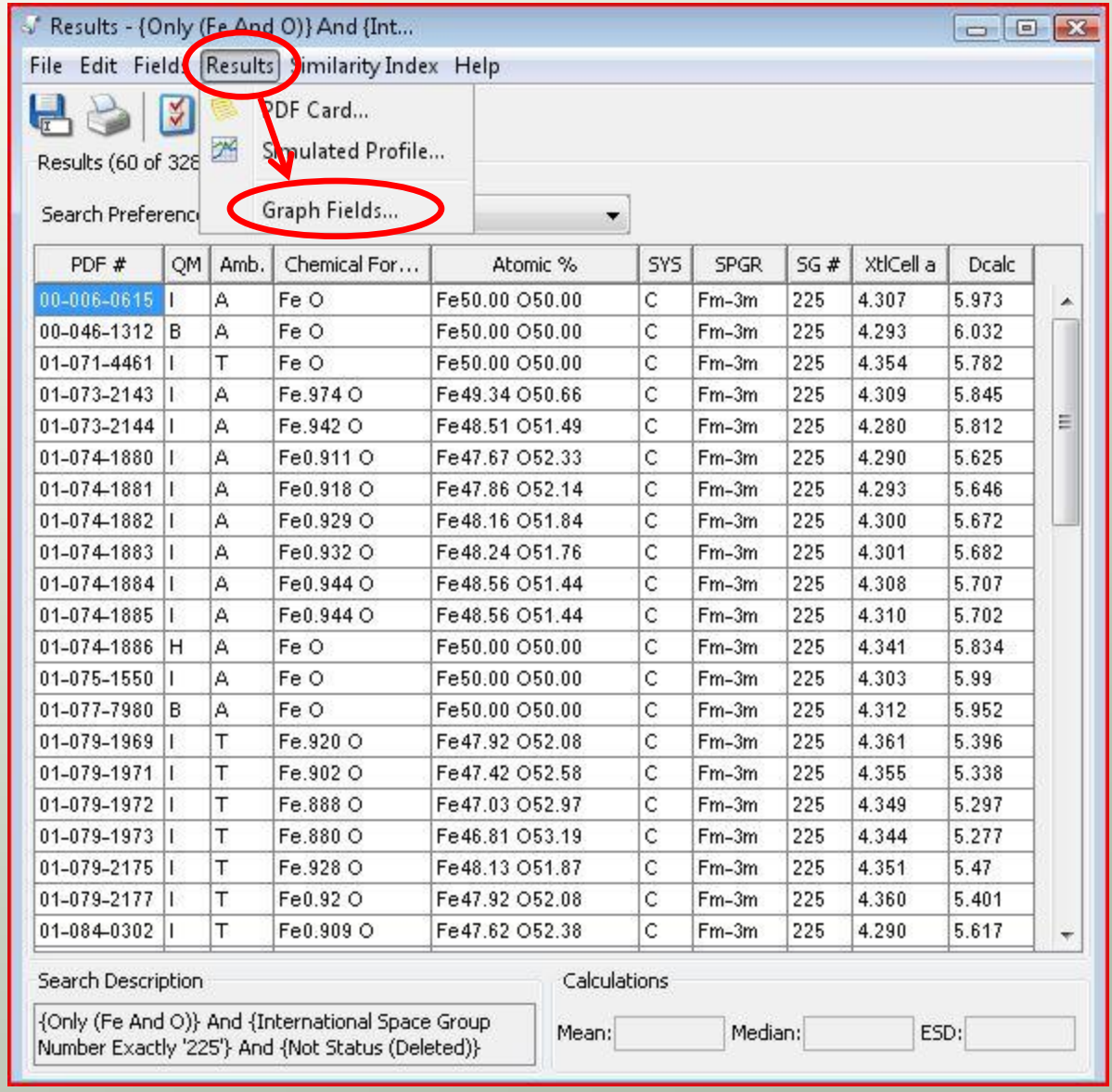
PDF #	QM	Amb.	Chemical For...	Atomic %	SYS	SPGR	SG #	XtlCell a	Dcalc
00-006-0615	I	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.307	5.973
00-046-1312	B	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.293	6.032
01-071-4461	I	T	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.354	5.782
01-073-2143	I	A	Fe.974 O	Fe49.34 O50.66	C	Fm-3m	225	4.309	5.845
01-073-2144	I	A	Fe.942 O	Fe48.51 O51.49	C	Fm-3m	225	4.280	5.812
01-074-1880	I	A	Fe0.911 O	Fe47.67 O52.33	C	Fm-3m	225	4.290	5.625
01-074-1881	I	A	Fe0.918 O	Fe47.86 O52.14	C	Fm-3m	225	4.293	5.646
01-074-1882	I	A	Fe0.929 O	Fe48.16 O51.84	C	Fm-3m	225	4.300	5.672
01-074-1883	I	A	Fe0.932 O	Fe48.24 O51.76	C	Fm-3m	225	4.301	5.682
01-074-1884	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.308	5.707
01-074-1885	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.310	5.702
01-074-1886	H	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.341	5.834
01-075-1550	I	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.303	5.99
01-077-7980	B	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.312	5.952
01-079-1969	I	T	Fe.920 O	Fe47.92 O52.08	C	Fm-3m	225	4.361	5.396
01-079-1971	I	T	Fe.902 O	Fe47.42 O52.58	C	Fm-3m	225	4.355	5.338
01-079-1972	I	T	Fe.888 O	Fe47.03 O52.97	C	Fm-3m	225	4.349	5.297
01-079-1973	I	T	Fe.880 O	Fe46.81 O53.19	C	Fm-3m	225	4.344	5.277
01-079-2175	I	T	Fe.928 O	Fe48.13 O51.87	C	Fm-3m	225	4.351	5.47
01-079-2177	I	T	Fe0.92 O	Fe47.92 O52.08	C	Fm-3m	225	4.360	5.401
01-084-0302	I	T	Fe0.909 O	Fe47.62 O52.38	C	Fm-3m	225	4.290	5.617

Analysis of the Resulting Database Entries

Most fields in the results table can be graphically illustrated in either X-Y plot or histogram form.

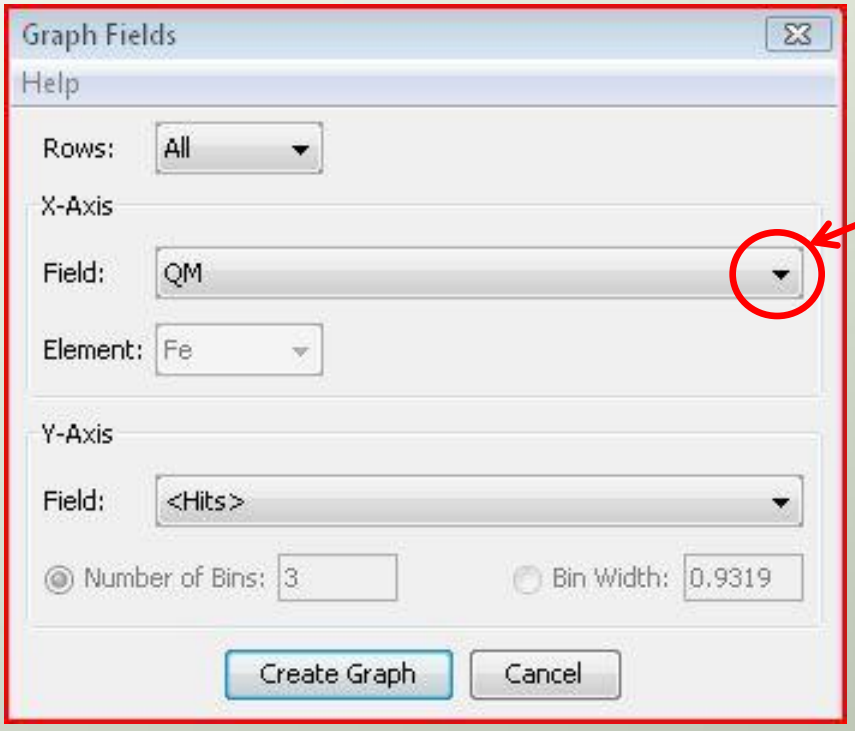
For the current application, we will use an X-Y plot to illustrate the a-axis cell parameter as a function of atomic % Fe.

To do this, ‘Graph Fields…’ is first selected from the ‘Results’ drop down menu of the ‘Results’ window.



The ‘Graph Fields’ Selection Box

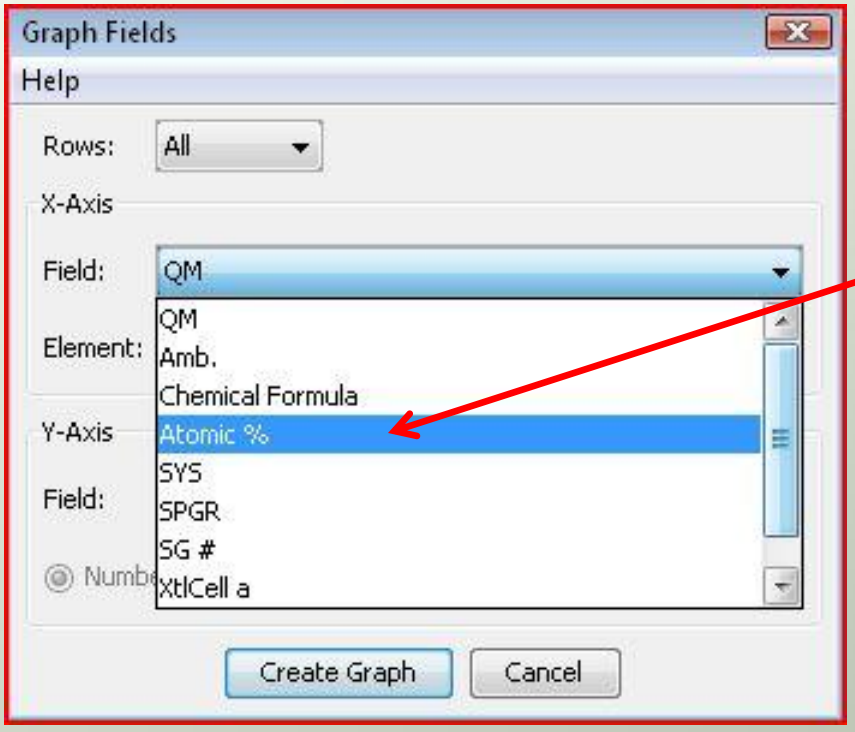
Here the types of data to plot on the x- and y-axes of the graph are selected.



To select the type of data for the x-axis, use the drop-down menu here.

The ‘Graph Fields’ Selection Box

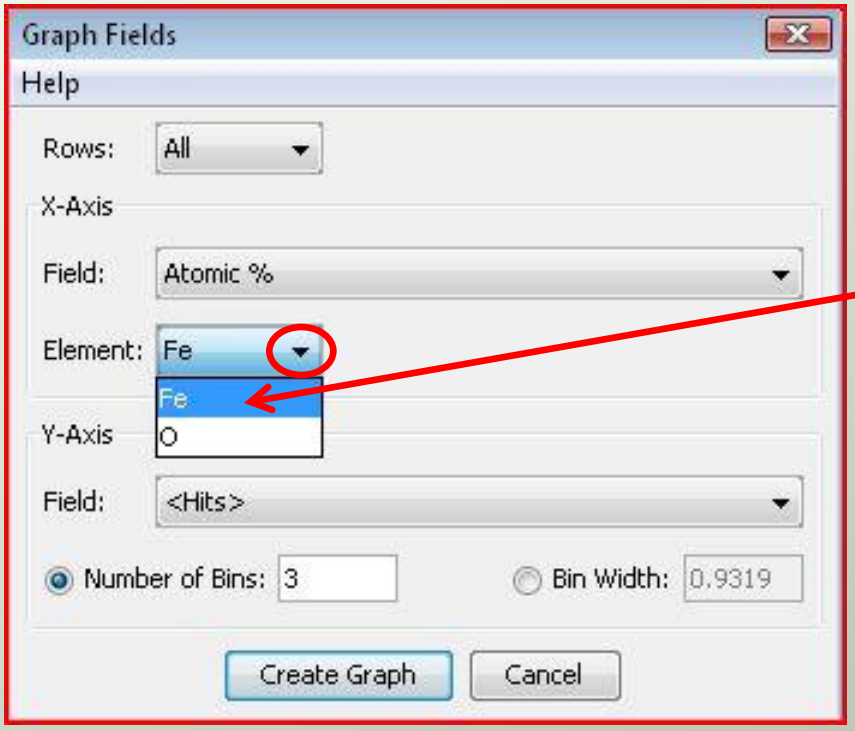
Here the types of data to plot on the x- and y-axes of the graph are selected.



For this graph, we will choose ‘Atomic %’ for the X-axis.

The ‘Graph Fields’ Selection Box

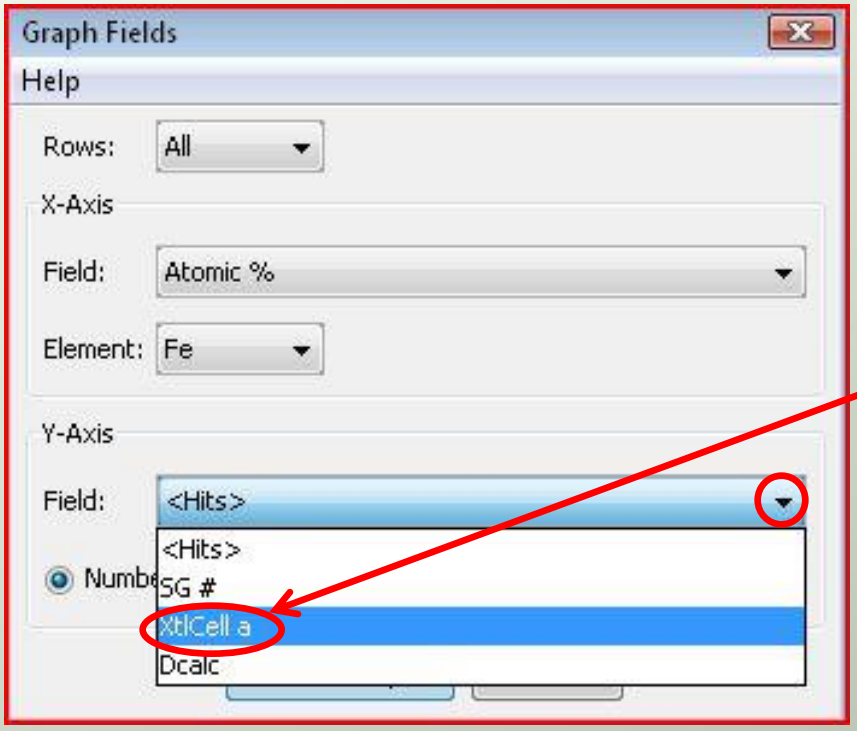
Here the types of data to plot on the x- and y-axes of the graph are selected.



Now we select the element whose atomic % is to be plotted – in this case, ‘Fe’.

The ‘Graph Fields’ Selection Box

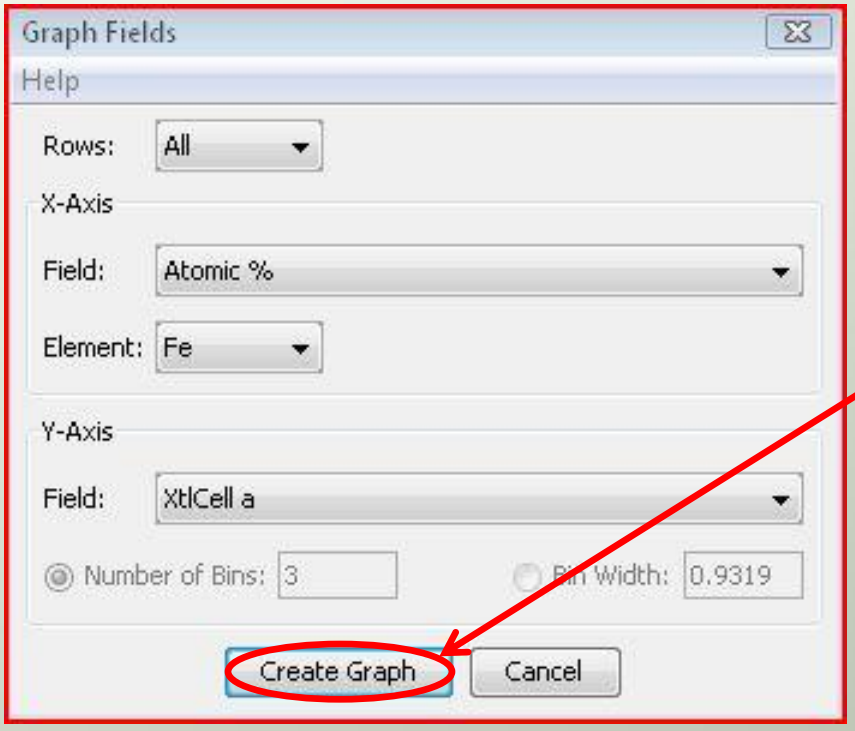
Here the types of data to plot on the x- and y-axes of the graph are selected.



Next we select the data to be plotted along the y-axis, namely ‘XtlCell a’.

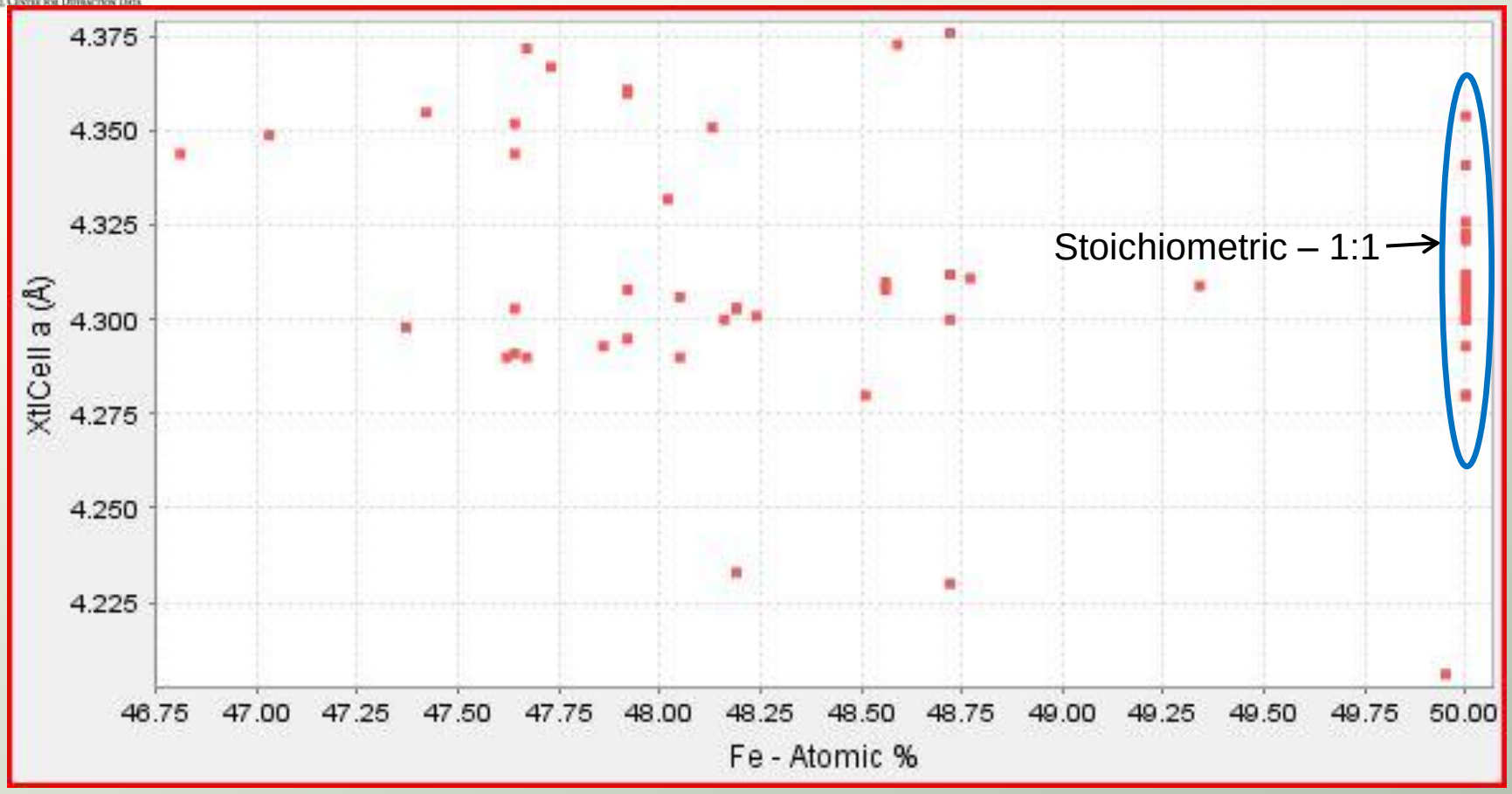
The ‘Graph Fields’ Selection Box

Here the types of data to plot on the x- and y-axes of the graph are selected.



Click on ‘Create Graph’ to display the graph.

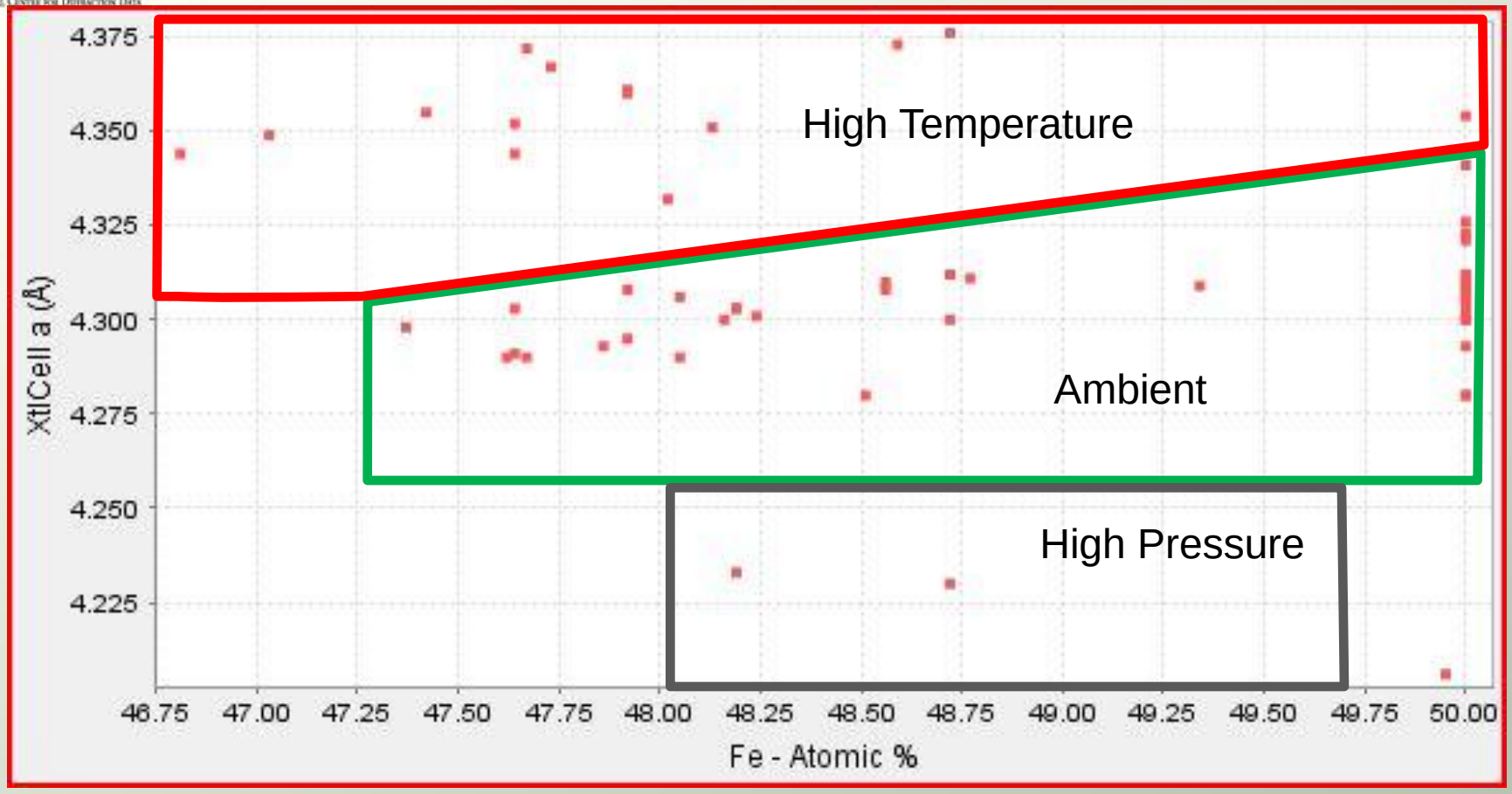
FeO a-axis Cell Parameter vs. Atomic % Fe



This graph shows little apparent correlation between atomic % Fe and a-axis.

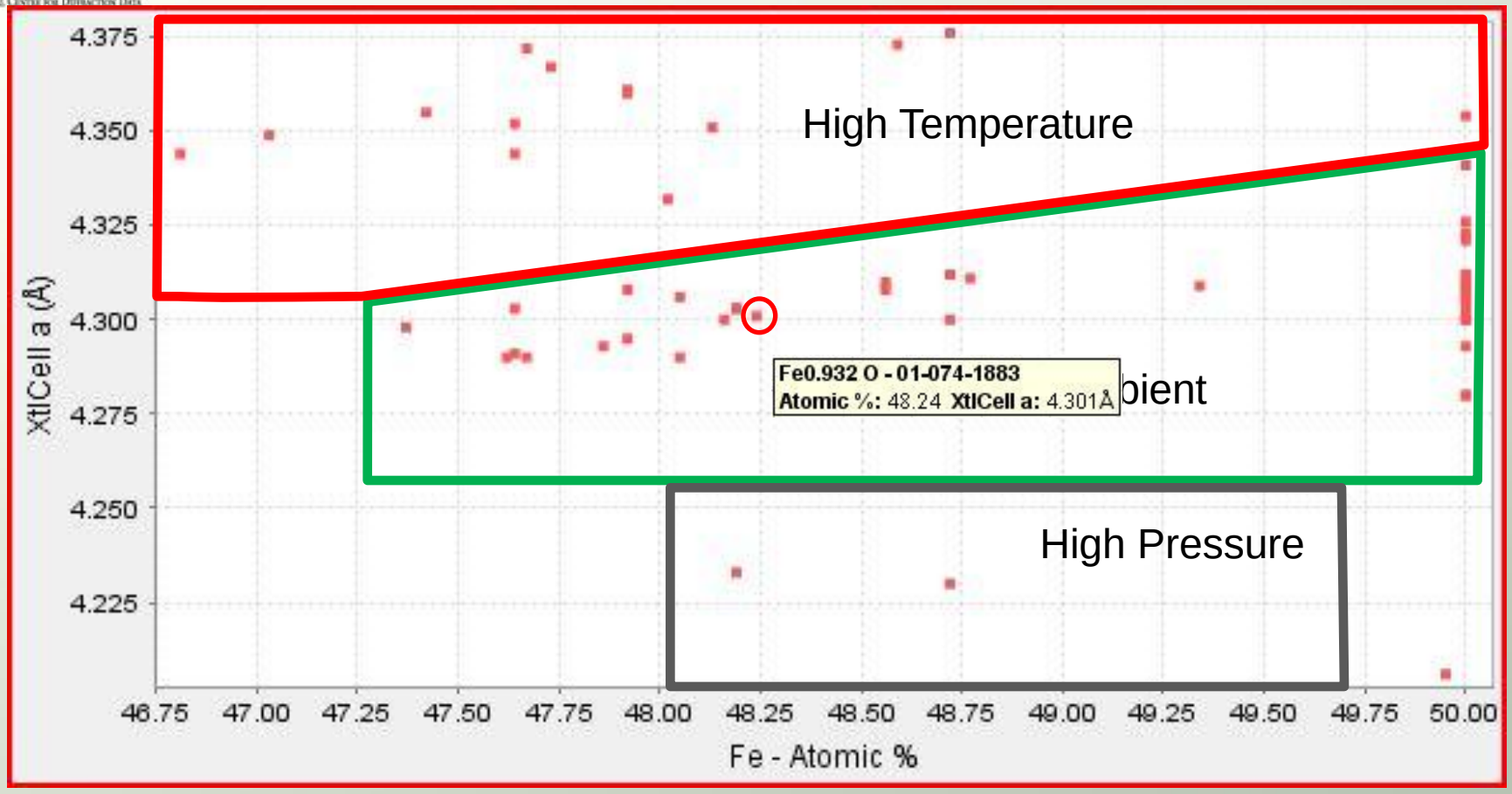
Note that entries *reported* as being stoichiometric (1:1) are in a vertical line at right (50 at.% Fe). All others report less than stoichiometric amounts of Fe.

FeO a-axis Cell Parameter vs. Atomic % Fe



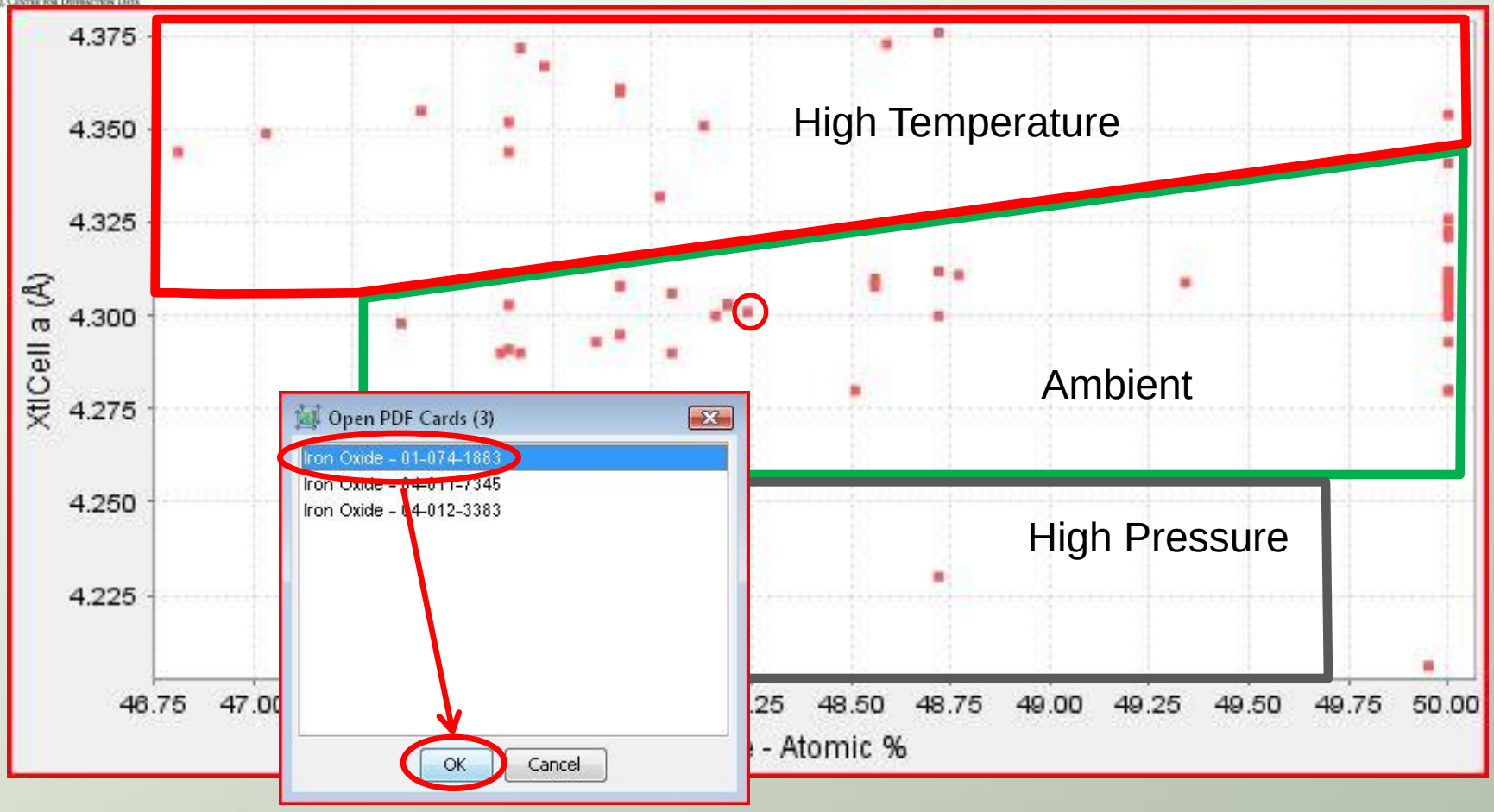
Further examination of individual entries separates ambient, high-temperature, and high-pressure determinations of the a-axis.

FeO a-axis Cell Parameter vs. Atomic % Fe



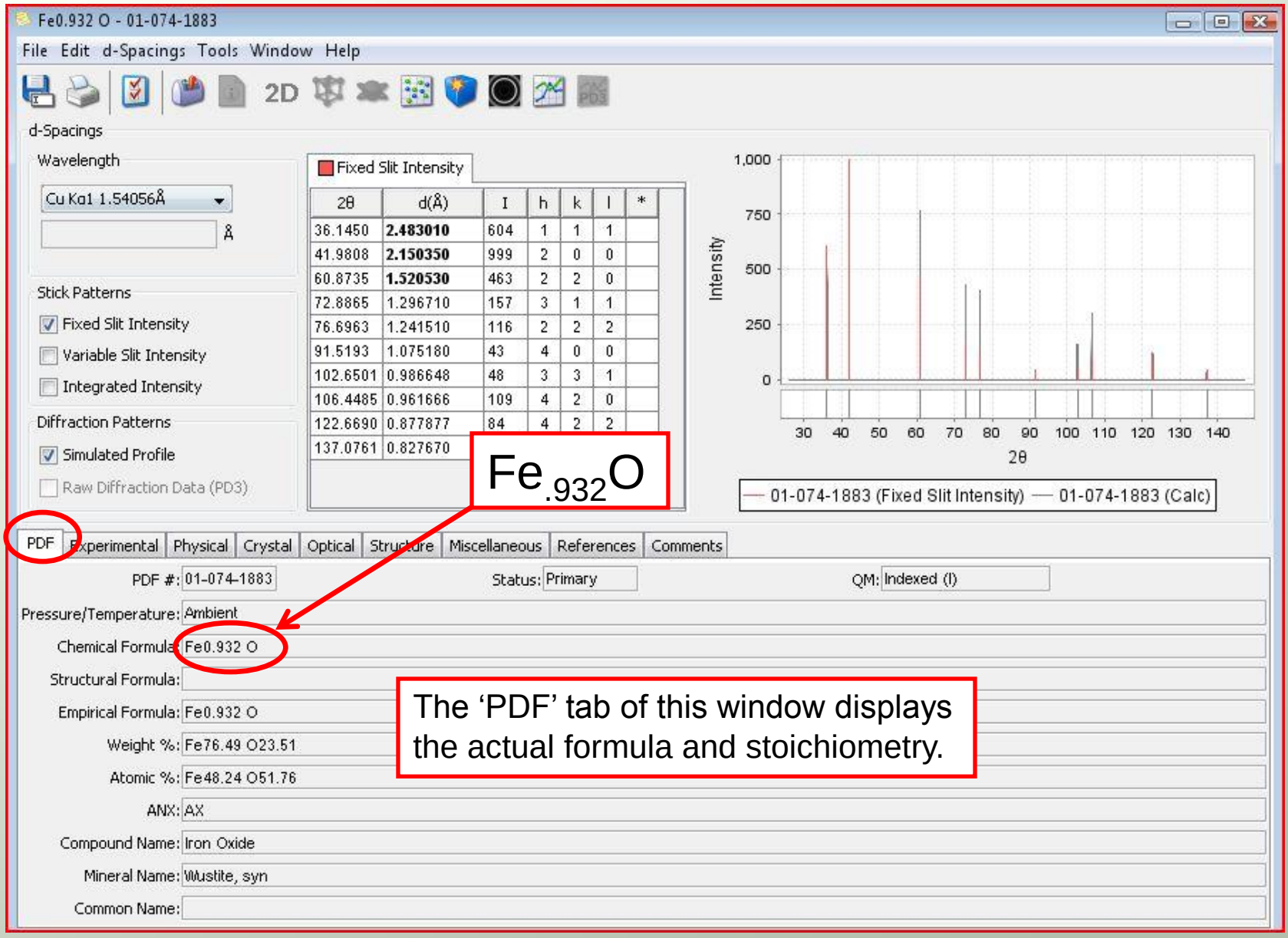
- Individual entries from this chart may be examined by left-clicking on individual spots. The illustration above shows the point label that appears when the mouse cursor is ‘hovered’ over this data point.

FeO a-axis Cell Parameter vs. Atomic % Fe



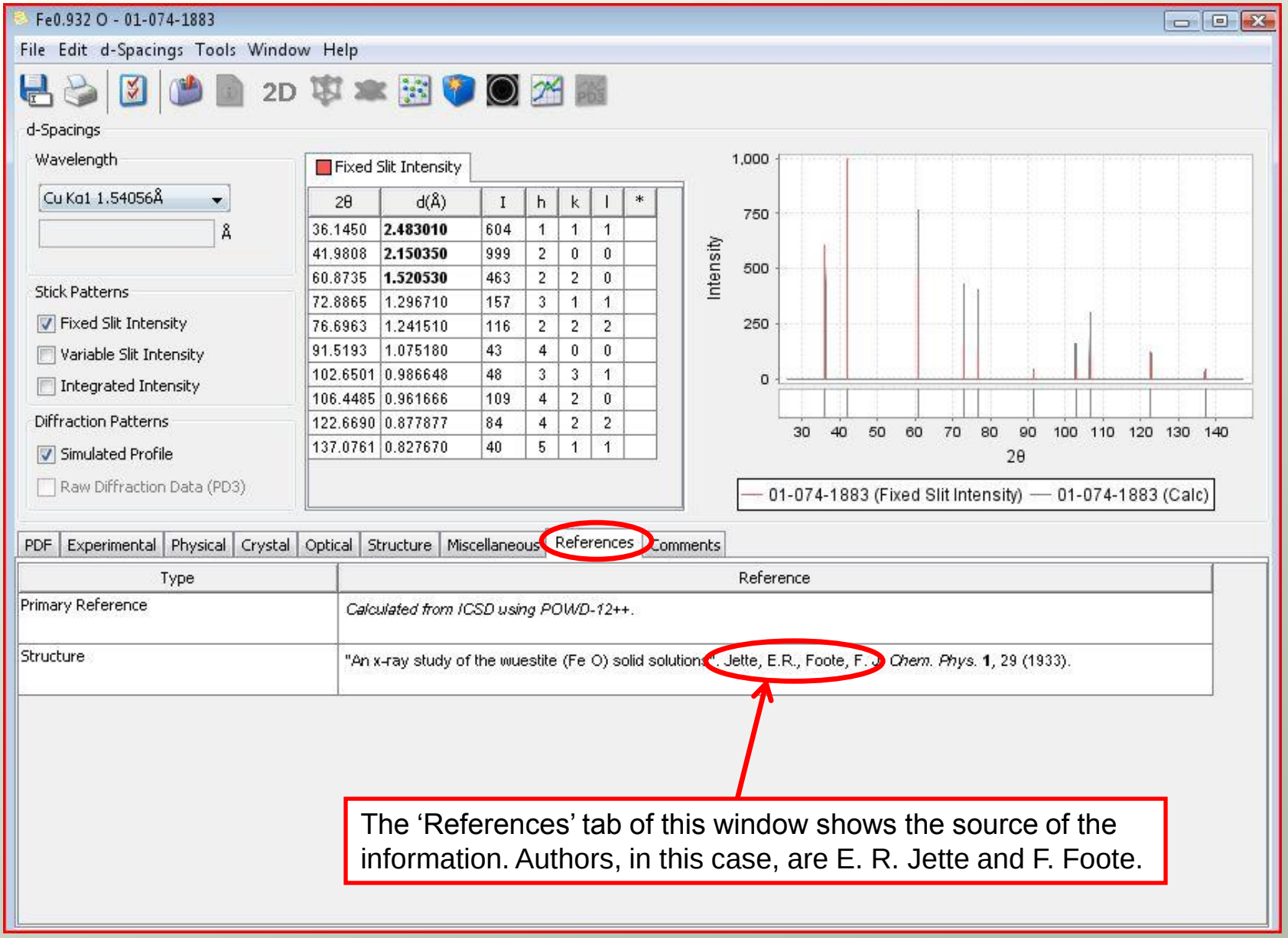
- If you left-click at this point, depending on the proximity of nearby points on the graph, you may directly bring up the 01-074-1883 entry, or bring up a list of the nearby points as shown above. In the latter case, the point of interest is selected from the list and then 'OK' is clicked. This entry is shown on the next slide.

PDF Card for FeO (01-074-1883)



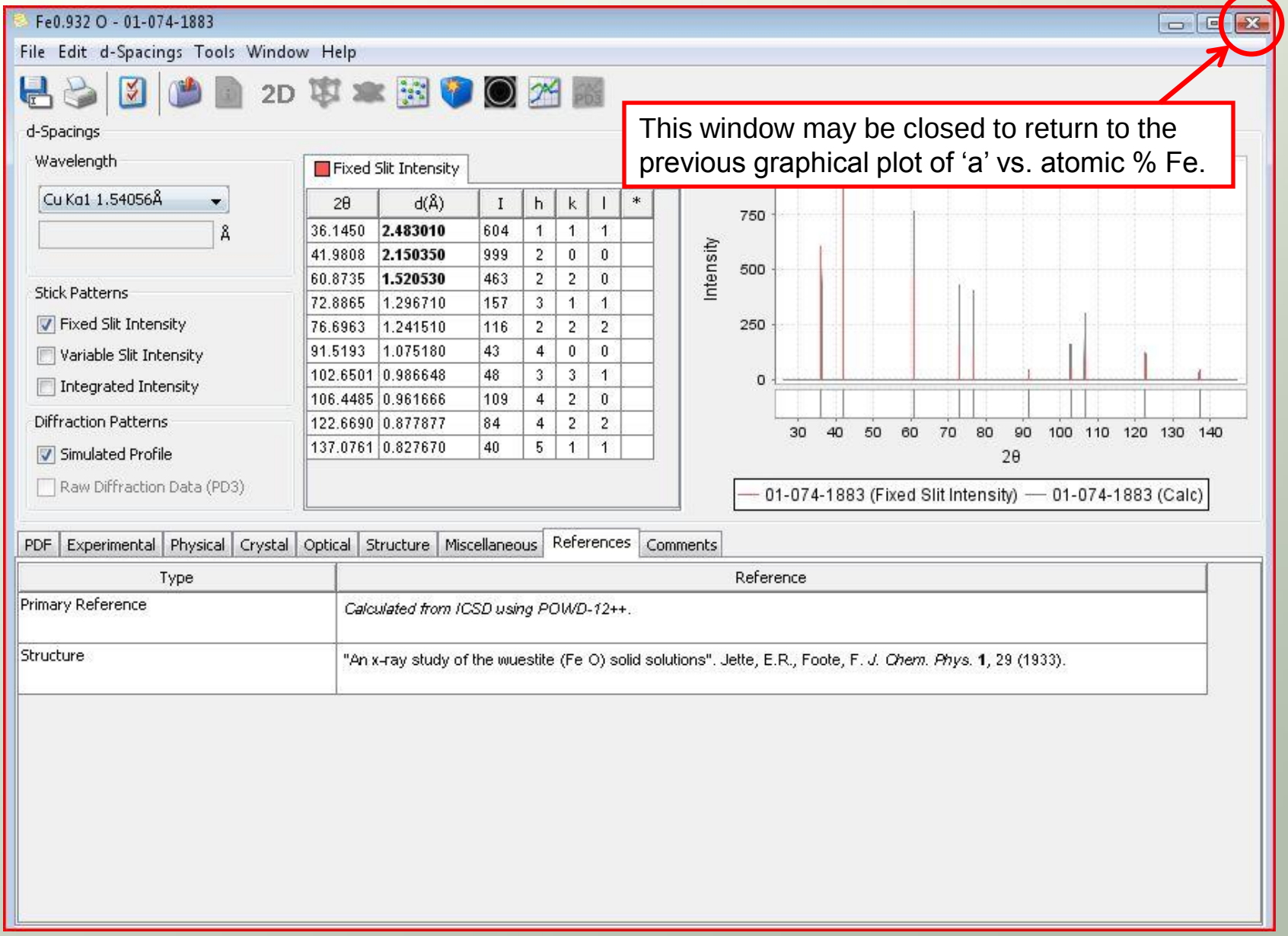
The ‘PDF’ tab of this window displays the actual formula and stoichiometry.

PDF Card for FeO (01-074-1883)

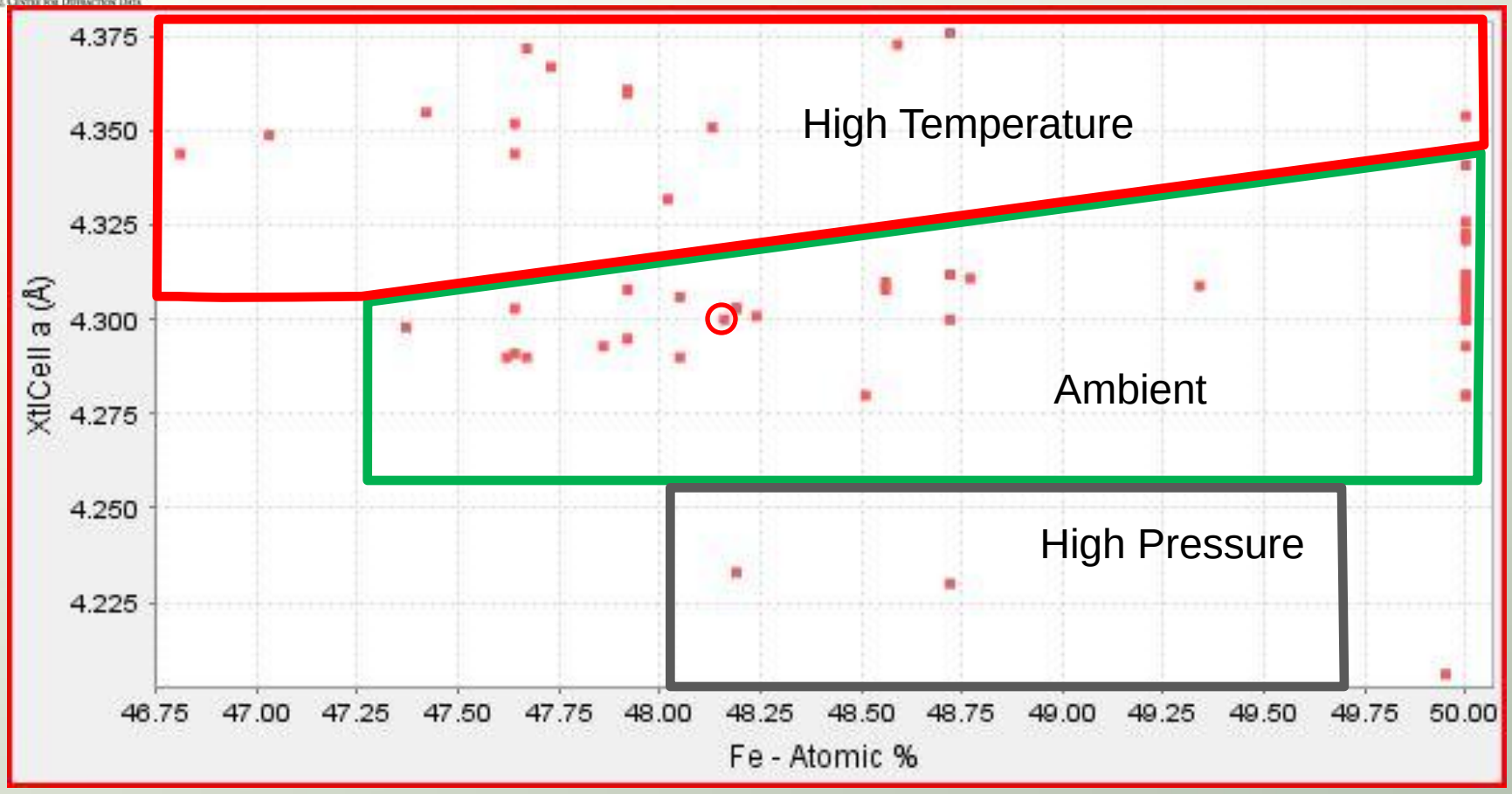


The ‘References’ tab of this window shows the source of the information. Authors, in this case, are E. R. Jette and F. Foote.

PDF Card for FeO (01-074-1883)



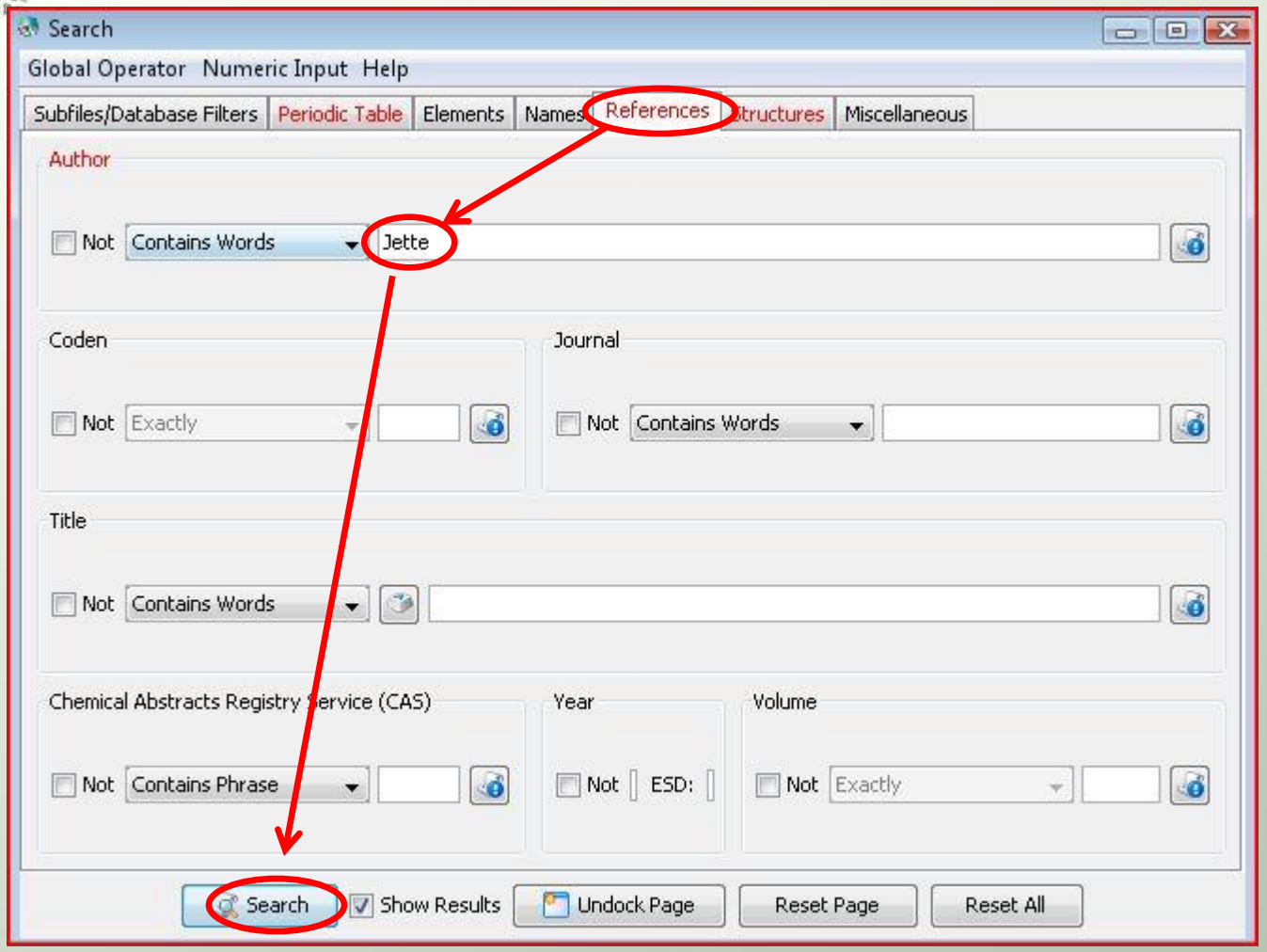
FeO a-axis Cell Parameter vs. Atomic % Fe



Examining another nearby point, corresponding to entry 01-074-1882, we note that the reference lists the same authors, E. R. Jette and F. Foote.

There may be other entries across the range of stoichiometries that are based on these authors' work. We can add an author's name to the search criteria to examine just their entries.

Adding an Author to the Search

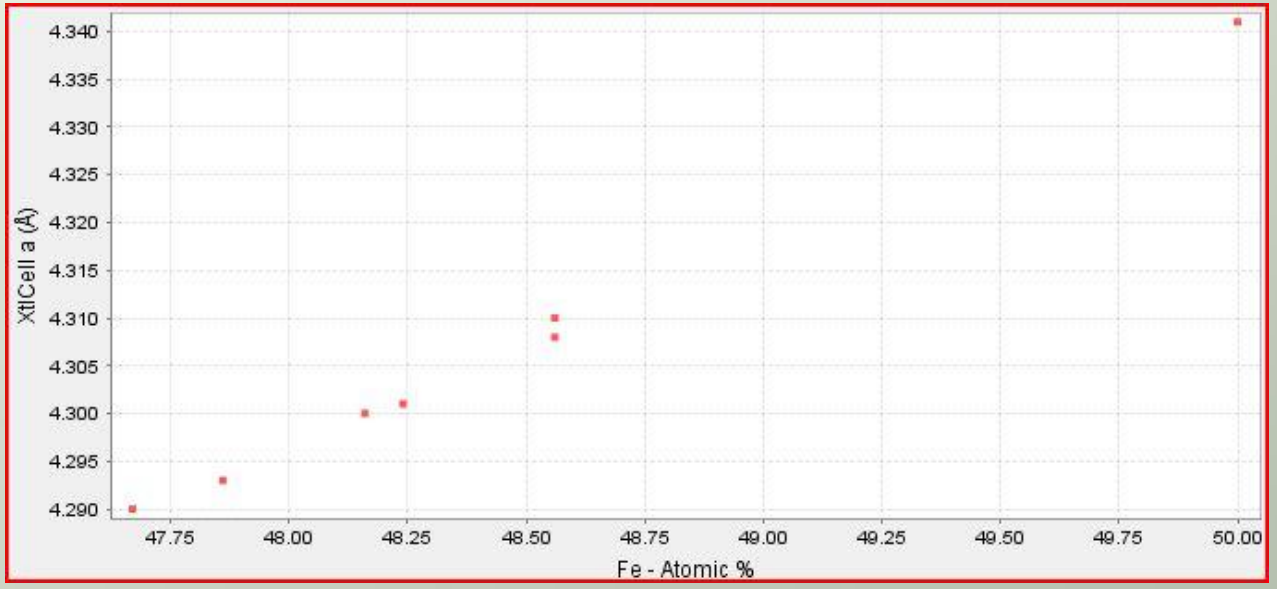


Without resetting the previous search criteria, we can add an author to the previous Periodic Table (Only Fe and O) and Structure (Space Group 225) specifications. Adding 'Jette' to the 'Author' box, and clicking 'Search' gives the Results list on the next slide:

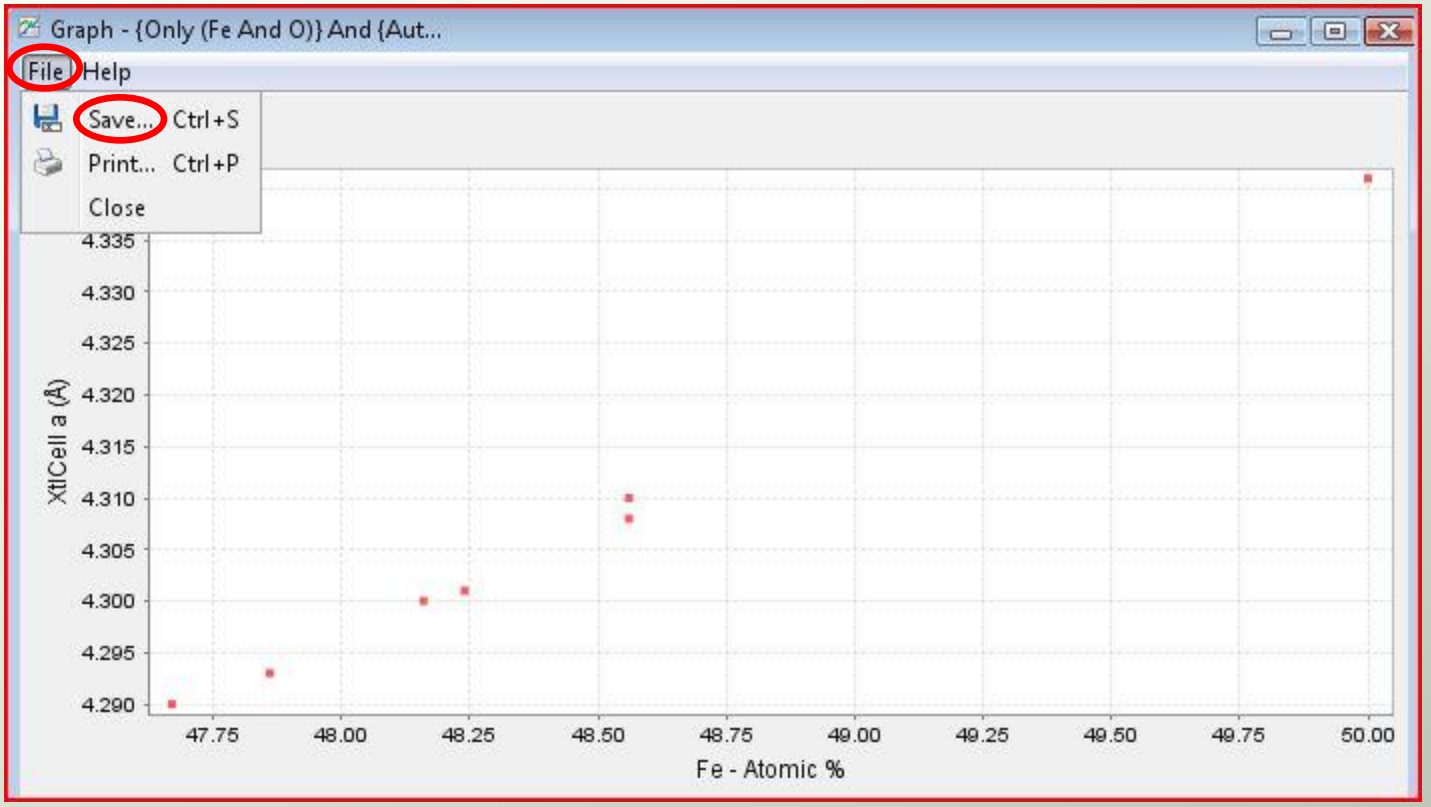
Search Result Including ‘Jette’ as Author

PDF #	QM	Amb.	Chemical For…	Atomic %	SYS	SPGR	SG #	XtlCell a	Dcalc
01-074-1880	I	A	Fe0.911 O	Fe47.67 O52.33	C	Fm-3m	225	4.290	5.625
01-074-1881	I	A	Fe0.918 O	Fe47.86 O52.14	C	Fm-3m	225	4.293	5.646
01-074-1882	I	A	Fe0.929 O	Fe48.16 O51.84	C	Fm-3m	225	4.300	5.672
01-074-1883	I	A	Fe0.932 O	Fe48.24 O51.76	C	Fm-3m	225	4.301	5.682
01-074-1884	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.308	5.707
01-074-1885	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.310	5.702
01-074-1886	H	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.341	5.834

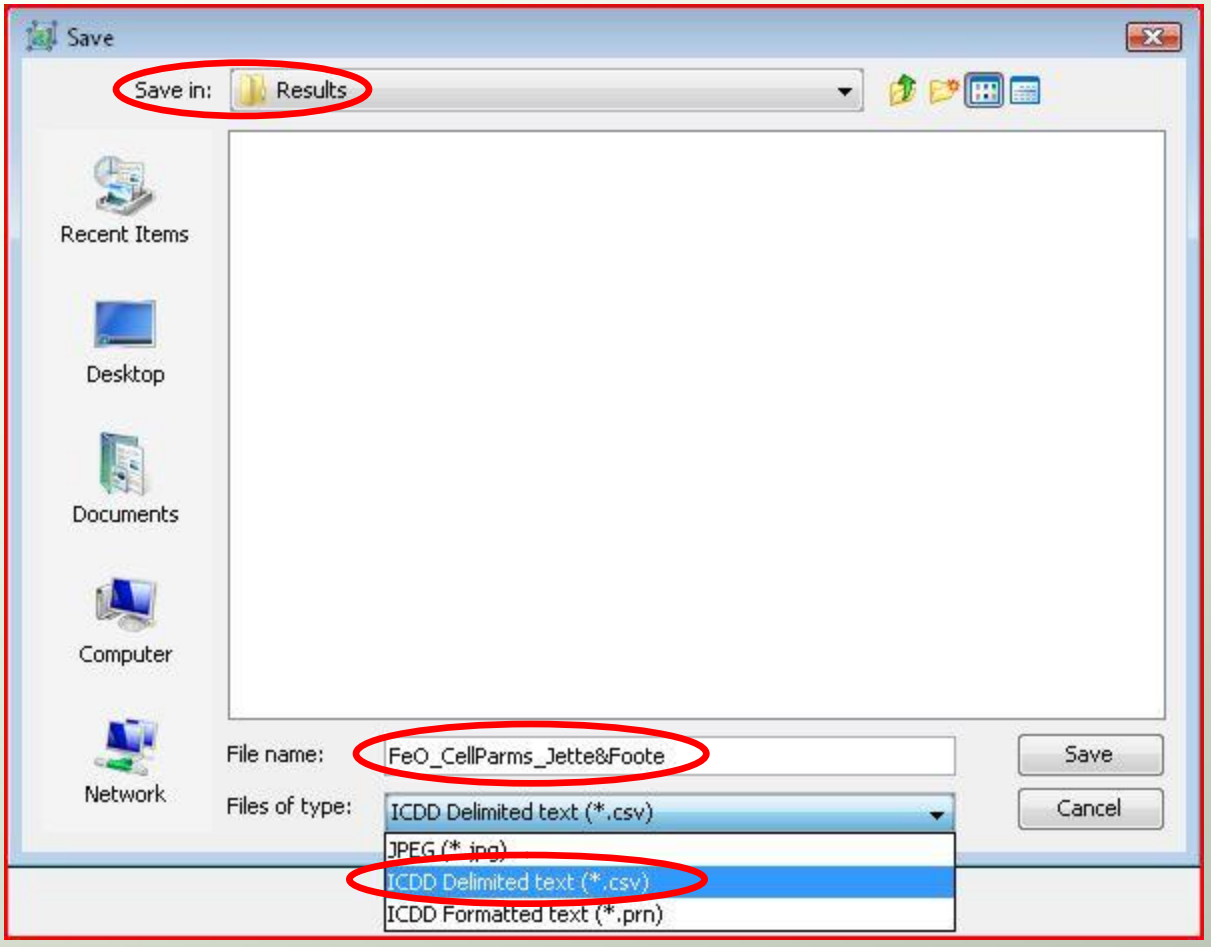
These results can be graphed as before . . .



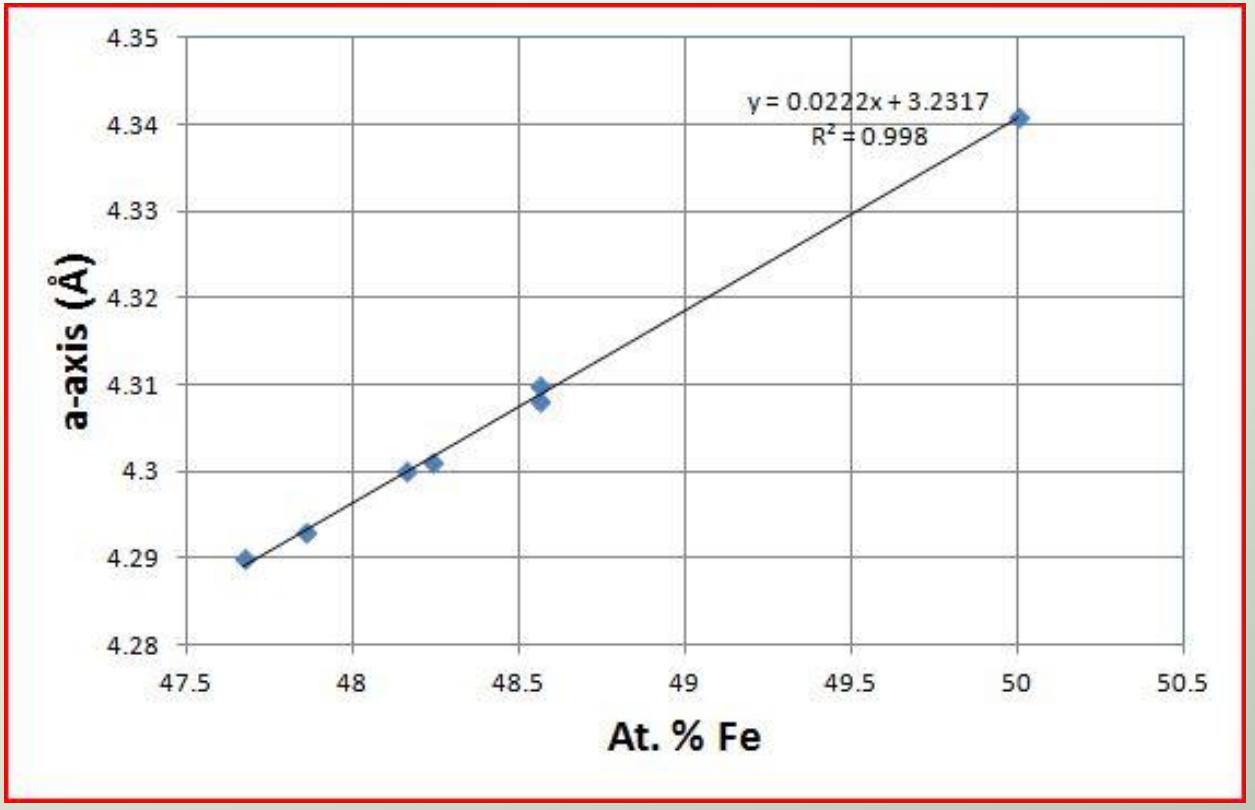
These represent the results of one systematic study of stoichiometry vs. structure published by Jette & Foote in *J. Chem. Phys.*



The underlying numerical values from this resulting graph can be exported for analysis by other software programs such as Microsoft® Excel®. From the 'File' menu on this graph, 'Save…' is selected.



The values can be saved to a ‘CSV’ (comma separated values) file for import into many other software analysis programs. The file name and folder are specified here as well.

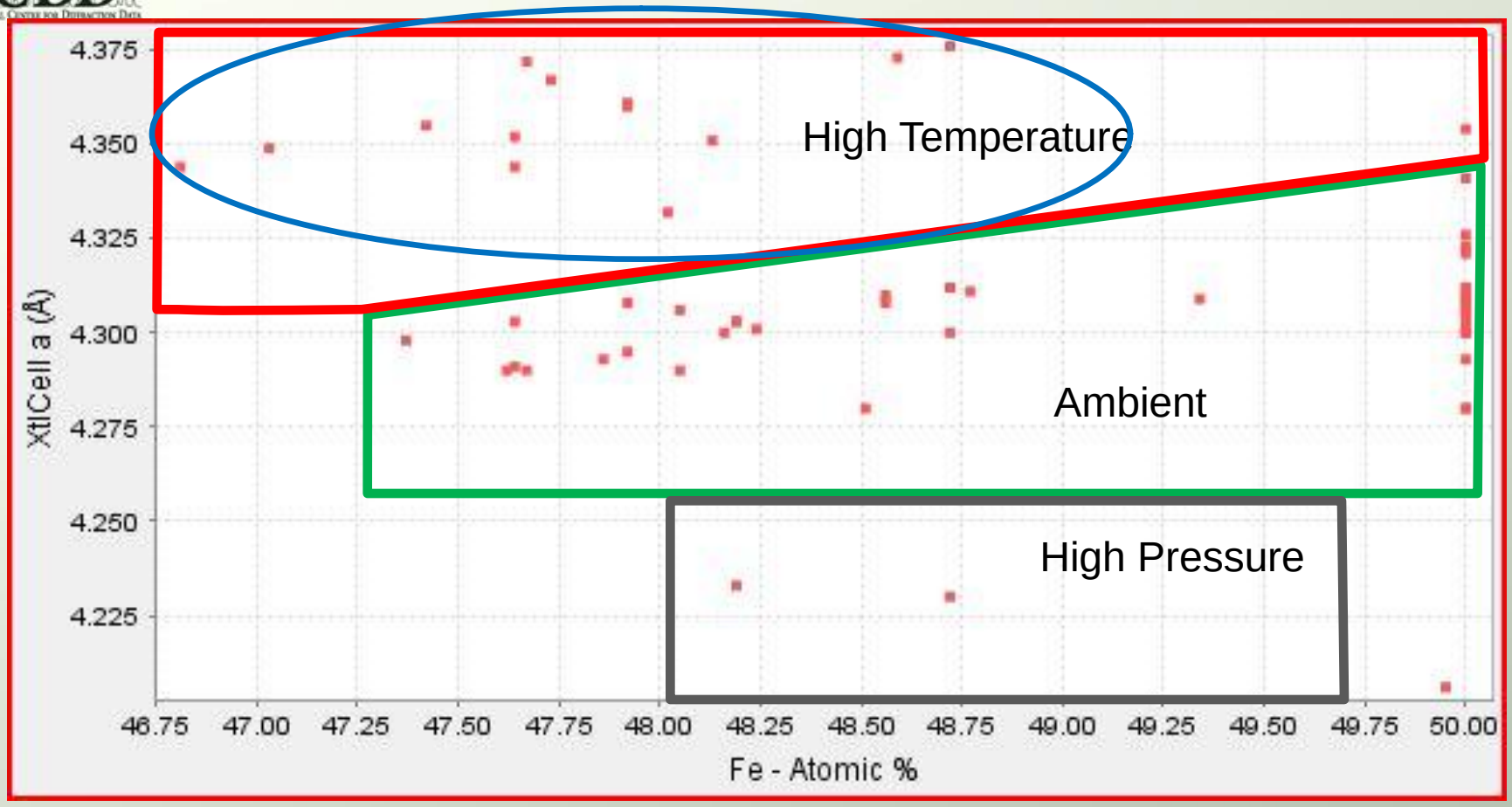


An example of a Microsoft® Excel® analysis of the Jette & Foote data. The linear analysis equation can be rearranged to give . . .

At. % Fe = 45.05 * a-axis (Å) - 145.6

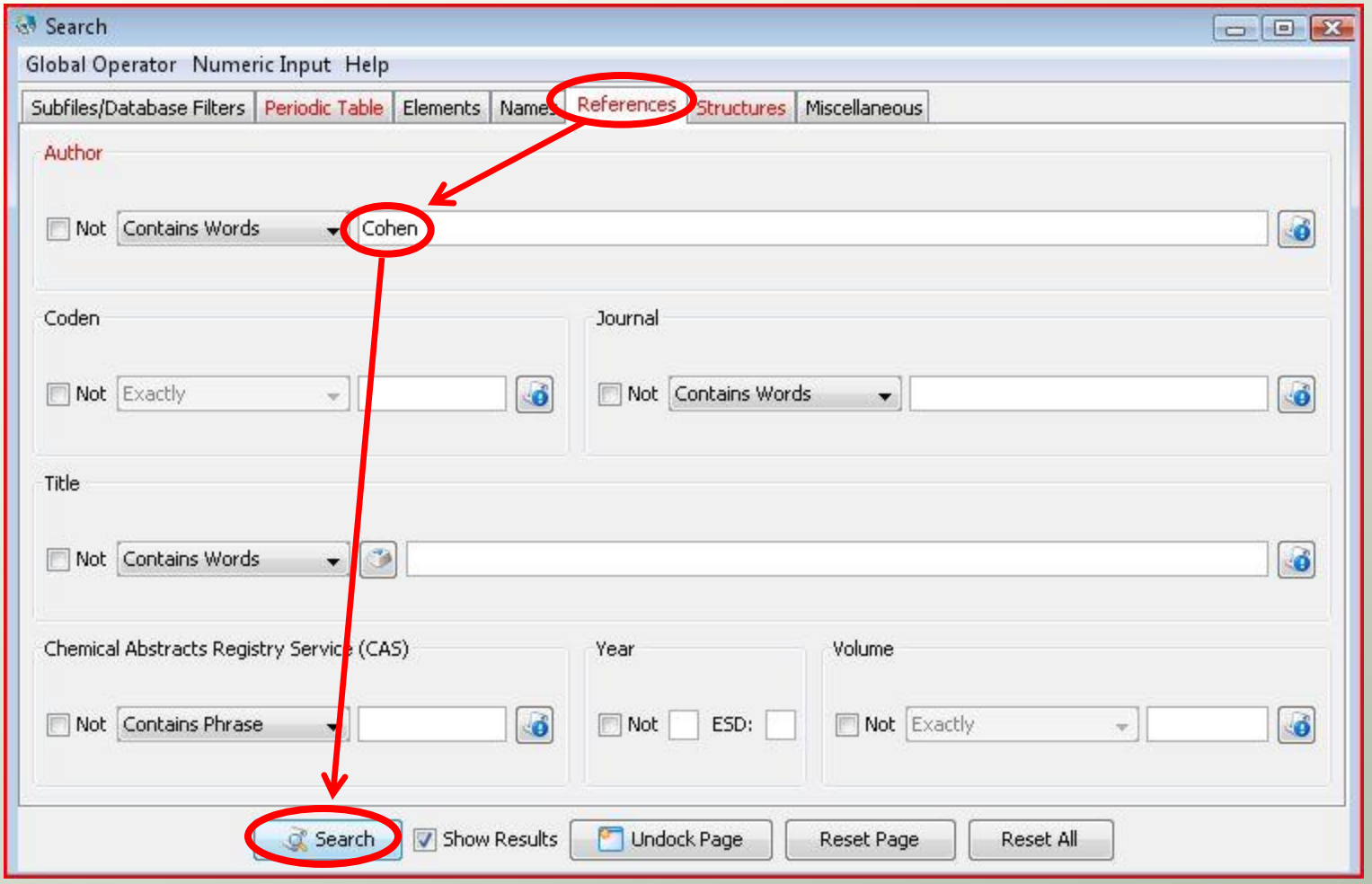
This would allow one to calculate the atomic % Fe from a measured a-axis value.

FeO a-axis Cell Parameter vs. Atomic % Fe



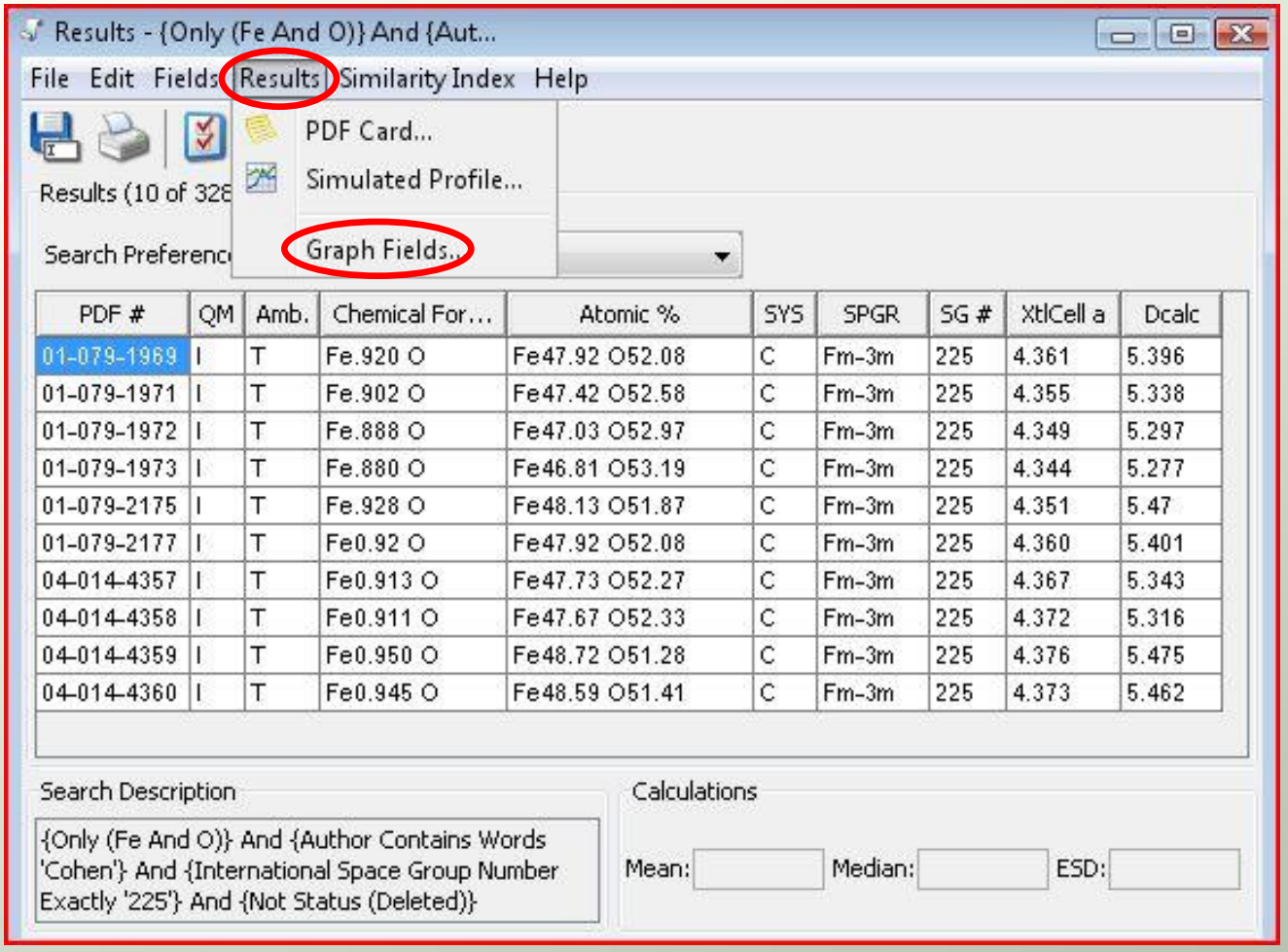
Several entries in the 'High Temperature' region of the original results graph come from a single study, "Point Defect Clusters in Wuestite" by Radler, Cohen, & Faber, *J. Phys. Chem. Solids*, 51, 217 (1990). We can again use the author criterion to look at just these entries.

Change Author for Search



On the ‘References’ tab, ‘Cohen’ has been entered in the ‘Author’ field to obtain the desired PDF entries. The ‘Structures’ and ‘Periodic Table’ tabs contain the previously entered information regarding FeO and space group 225. This search will yield the 10 entries found on the next slide.

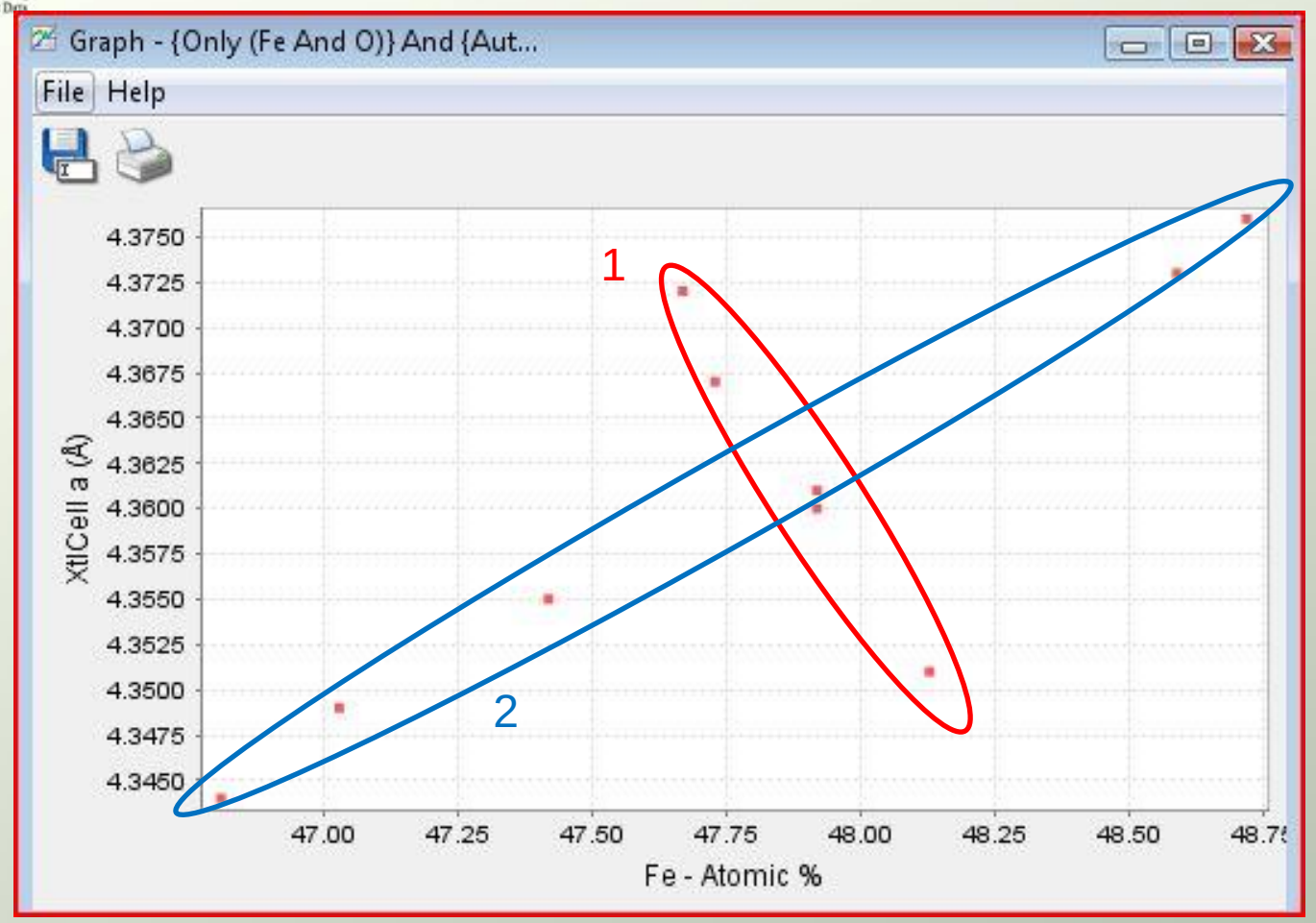
PDF Entries from Radler, Cohen, & Faber Study (1990)



PDF #	QM	Amb.	Chemical For...	Atomic %	SYS	SPGR	SG #	XtlCell a	Dcalc
01-079-1969	I	T	Fe.920 O	Fe47.92 O52.08	C	Fm-3m	225	4.361	5.396
01-079-1971	I	T	Fe.902 O	Fe47.42 O52.58	C	Fm-3m	225	4.355	5.338
01-079-1972	I	T	Fe.888 O	Fe47.03 O52.97	C	Fm-3m	225	4.349	5.297
01-079-1973	I	T	Fe.880 O	Fe46.81 O53.19	C	Fm-3m	225	4.344	5.277
01-079-2175	I	T	Fe.928 O	Fe48.13 O51.87	C	Fm-3m	225	4.351	5.47
01-079-2177	I	T	Fe0.92 O	Fe47.92 O52.08	C	Fm-3m	225	4.360	5.401
04-014-4357	I	T	Fe0.913 O	Fe47.73 O52.27	C	Fm-3m	225	4.367	5.343
04-014-4358	I	T	Fe0.911 O	Fe47.67 O52.33	C	Fm-3m	225	4.372	5.316
04-014-4359	I	T	Fe0.950 O	Fe48.72 O51.28	C	Fm-3m	225	4.376	5.475
04-014-4360	I	T	Fe0.945 O	Fe48.59 O51.41	C	Fm-3m	225	4.373	5.462

The a-axis cell parameter for just these resulting 10 entries can now be plotted vs. atomic % Fe and the resulting graph is shown on the following slide.

Graph of Radler, Cohen, and Faber FeO Entries



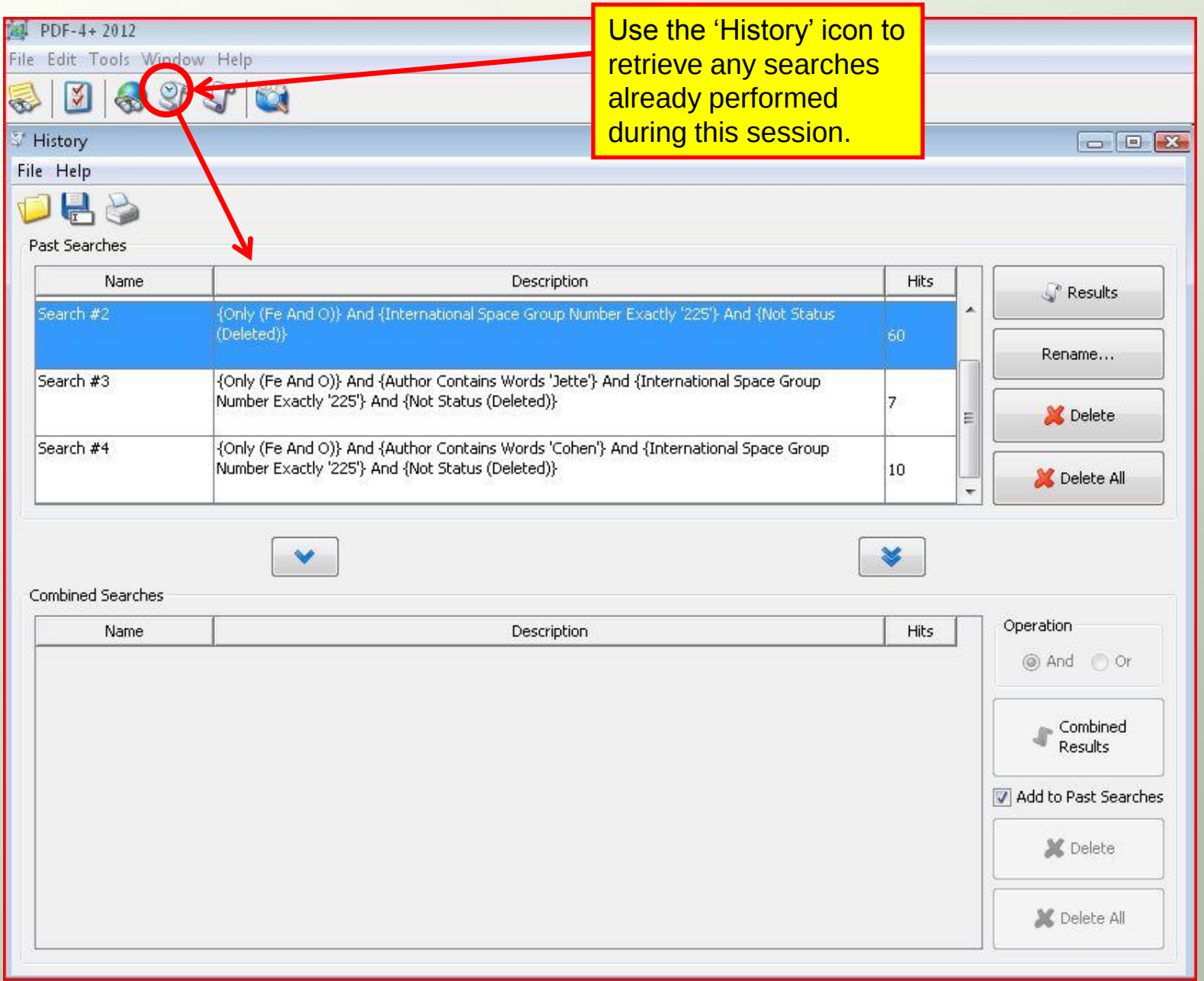
These points represent two sets of high-temperature X-ray data obtained in the referenced report as follows:

1. Data varying T from 1123 to 1373 C with slightly increasing O content

2. Data varying stoichiometry at 1323 C from $Fe_{0.88}O$ to $Fe_{0.95}O$

Another Look at FeO results - Density

Return to the original list of 63 FeO entries using ‘History’ . . .



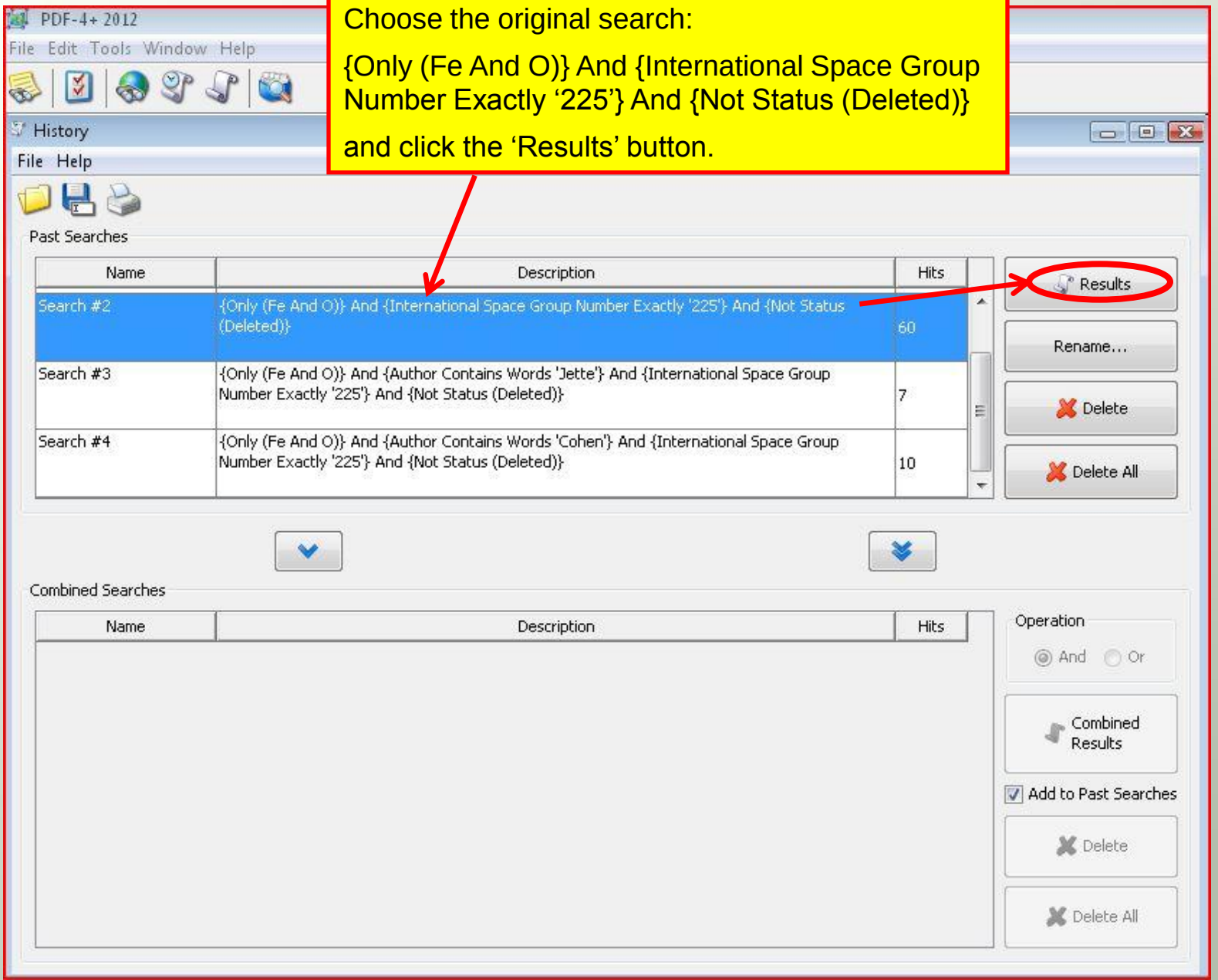
Another Look at FeO results - Density

Return to the original list of 60 FeO entries using 'History' . . .

Choose the original search:

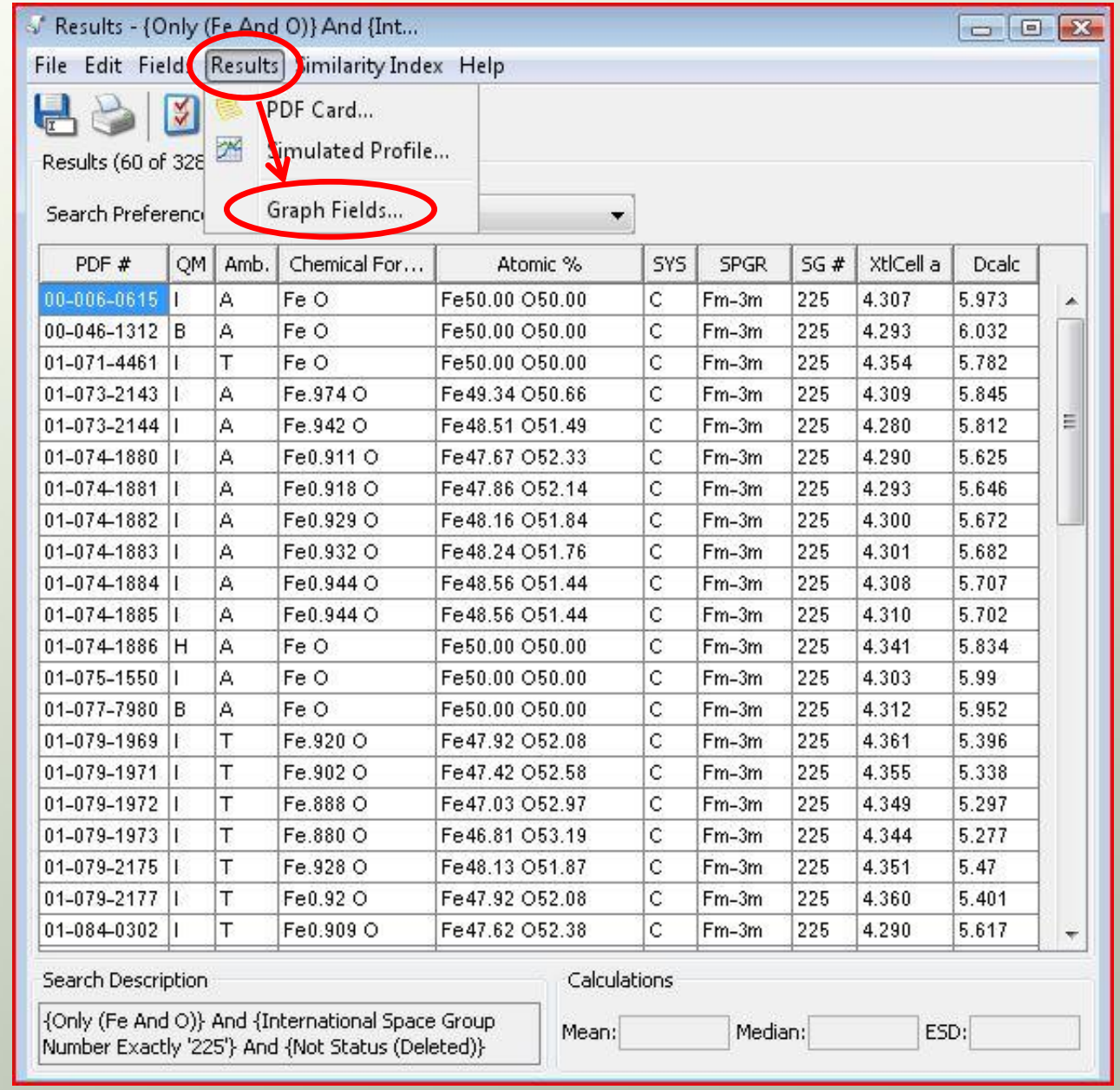
{Only (Fe And O)} And {International Space Group Number Exactly '225'} And {Not Status (Deleted)}

and click the 'Results' button.



Another Look at FeO results - Density

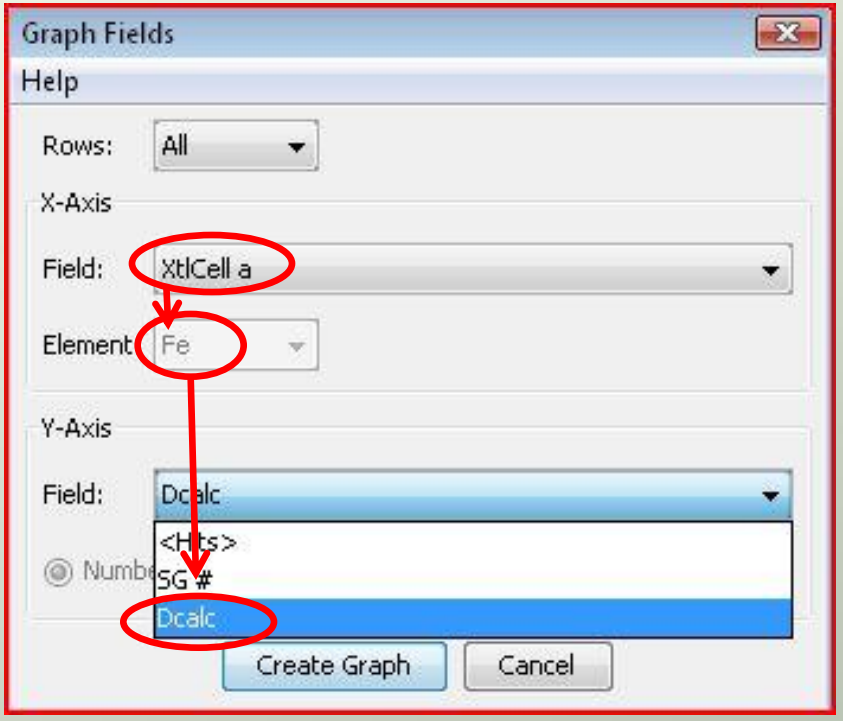
Another way to analyze this data is to look at the density as a function of cell parameter. This is performed by using the ‘Results’ drop down menu to access ‘Graph Fields…’



PDF #	QM	Amb.	Chemical For…	Atomic %	SYS	SPGR	SG #	XtlCell a	Dcalc
00-006-0615	I	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.307	5.973
00-046-1312	B	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.293	6.032
01-071-4461	I	T	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.354	5.782
01-073-2143	I	A	Fe.974 O	Fe49.34 O50.66	C	Fm-3m	225	4.309	5.845
01-073-2144	I	A	Fe.942 O	Fe48.51 O51.49	C	Fm-3m	225	4.280	5.812
01-074-1880	I	A	Fe0.911 O	Fe47.67 O52.33	C	Fm-3m	225	4.290	5.625
01-074-1881	I	A	Fe0.918 O	Fe47.86 O52.14	C	Fm-3m	225	4.293	5.646
01-074-1882	I	A	Fe0.929 O	Fe48.16 O51.84	C	Fm-3m	225	4.300	5.672
01-074-1883	I	A	Fe0.932 O	Fe48.24 O51.76	C	Fm-3m	225	4.301	5.682
01-074-1884	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.308	5.707
01-074-1885	I	A	Fe0.944 O	Fe48.56 O51.44	C	Fm-3m	225	4.310	5.702
01-074-1886	H	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.341	5.834
01-075-1550	I	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.303	5.99
01-077-7980	B	A	Fe O	Fe50.00 O50.00	C	Fm-3m	225	4.312	5.952
01-079-1969	I	T	Fe.920 O	Fe47.92 O52.08	C	Fm-3m	225	4.361	5.396
01-079-1971	I	T	Fe.902 O	Fe47.42 O52.58	C	Fm-3m	225	4.355	5.338
01-079-1972	I	T	Fe.888 O	Fe47.03 O52.97	C	Fm-3m	225	4.349	5.297
01-079-1973	I	T	Fe.880 O	Fe46.81 O53.19	C	Fm-3m	225	4.344	5.277
01-079-2175	I	T	Fe.928 O	Fe48.13 O51.87	C	Fm-3m	225	4.351	5.47
01-079-2177	I	T	Fe0.92 O	Fe47.92 O52.08	C	Fm-3m	225	4.360	5.401
01-084-0302	I	T	Fe0.909 O	Fe47.62 O52.38	C	Fm-3m	225	4.290	5.617

Another Look at FeO results - Density

For this graph, we will plot the calculated density as a function of the cubic cell parameter.



Results: density vs. a-axis cell parameter for reported FeO structures

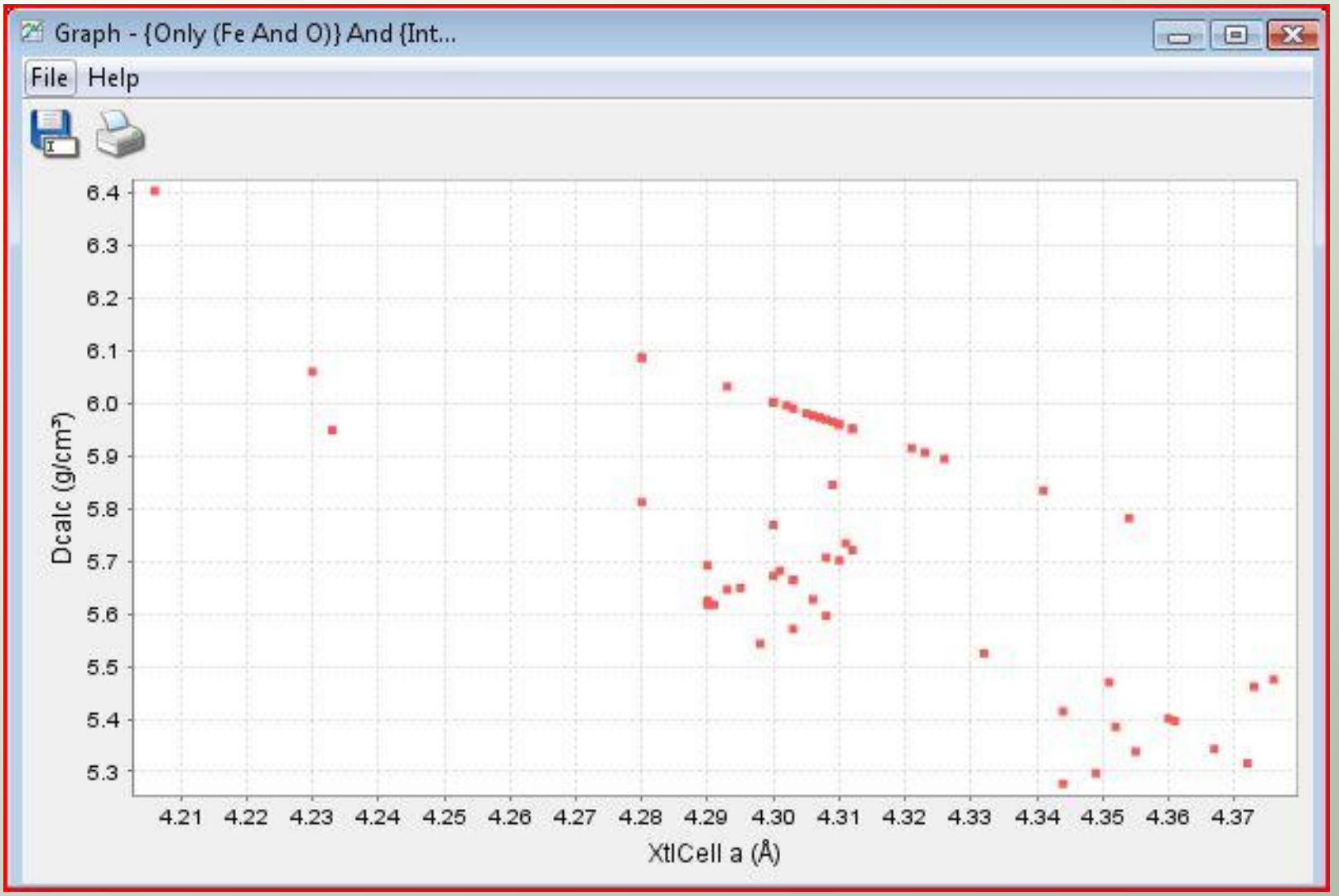
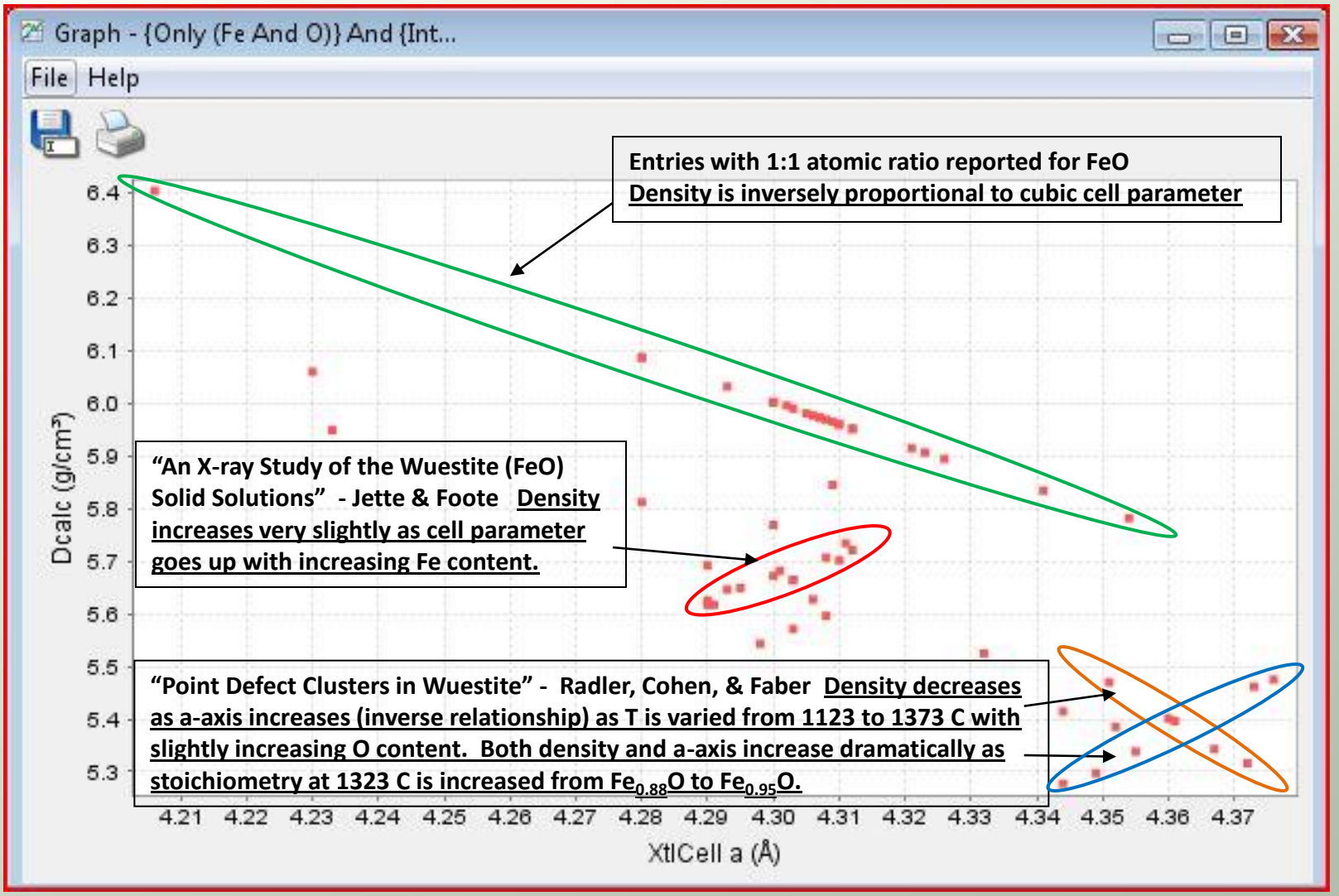


Illustration of correllations within this graph of density verses cell parameter for $Fe_{1-x}O$ data



Summary for Data Mining Non-stoichiometric Cubic FeO

- Multiple explanations exist for unit cell parameter variations in non-stoichiometric FeO in the PDF
- Systematic studies regarding stoichiometry and/or temperature can be “mined” from the database
- No single relationship describes all the data, thus different “defect” arrangements must exist for these materials
- Ability to access PDF entries directly from graphs’ facilitates obtaining other data and references

Thank you for viewing our tutorial.
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