

Supporting Information

Table. S1. Calculated magnetic moments of Ni in the 192, 12 and 48 atom unit cells of Li_xNiO_2 . The 192 atom cell shows occurrence of all three oxidized Ni cations Ni^{2+} , Ni^{3+} , Ni^{4+} in the delithiated structures, while in the 12 and 48 atom unit cells Ni is only Ni^{3+} .

S. No.	192 atom cell					12 atom cell	48 atom cell
	$x=0.25$ (Chain vacancy)	$x=0.5$ (Chain vacancy)	$x=0.75$ (Chain vacancy)	$x=0.75$ (Square vacancy)	$x=1$	$x=1$	$x=1$
	Magnetic moment (μ_B)	Magnetic moment (μ_B)	Magnetic moment (μ_B)	Magnetic moment (μ_B)	Magnetic moment (μ_B)	Magnetic moment (μ_B)	Magnetic moment (μ_B)
1-Ni	-0.0076	0.0736	0.8441	-0.0057	0.0643	1.0062	0.9897
2-Ni	0.0088	0.5042	1.5212	1.5397	1.4592	1.0062	0.9897
3-Ni	-0.0073	0.0494	0.0944	-0.0057	0.0643	1.0062	0.9897
4-Ni	-0.0035	0.7671	1.5212	1.5397	1.4592		0.9899
5-Ni	1.2196	0.7331	-0.0101	-0.0057	1.4095		0.9892
6-Ni	-0.0073	0.0849	-0.0101	0.8443	0.0643		0.9900
7-Ni	0.2268	0.0494	-0.0101	-0.0057	0.0643		0.990
8-Ni	-0.0084	0.7962	-0.0101	0.8443	1.4095		0.9900
9-Ni	-0.0031	0.0093	0.0944	1.5397	0.0999		0.9897
10-Ni	-0.0080	0.7331	1.5212	-0.0057	1.4095		0.9899
11-Ni	-0.0035	0.5042	0.8441	1.5397	1.4592		0.9897

12-Ni	-0.0084	0.7757	1.5212	-0.0057	1.4095		0.9897
13-Ni	-0.0080	0.7962	0.7998	0.8443	1.4095		
14-Ni	0.9368	0.0736	0.0213	-0.0057	0.0643		
15-Ni	-0.0076	0.1050	0.0213	0.8443	0.0643		
16-Ni	1.2196	0.7757	0.7998	-0.0057	1.4095		
17-Ni	0.0641	0.0093	0.0944	-0.0057	0.0998		
18-Ni	-0.0099	0.7757	1.5212	1.5397	1.4097		
19-Ni	0.7592	0.5042	0.8441	-0.0057	1.4590		
20-Ni	-0.0041	0.7331	1.5212	1.5397	1.4097		
21-Ni	-0.0099	0.7962	0.7999	0.8443	1.4097		
22-Ni	0.0798	0.0494	0.0213	-0.0057	0.0643		
23-Ni	-0.0111	0.0849	0.0213	0.8443	0.0643		
24-Ni	0.7501	0.7331	0.7999	-0.0057	1.4097		
25-Ni	-0.0188	0.0736	0.0944	1.5397	0.0643		
26-Ni	0.7592	0.7672	1.5212	-0.0057	1.4590		
27-Ni	-0.0111	0.0494	0.8440	1.5397	0.0643		
28-Ni	0.1490	0.5042	1.5212	-0.0057	1.4590		
29-Ni	0.0936	0.0736	-0.0101	-0.0057	0.0643		
30-Ni	-0.0041	0.7962	-0.0101	0.8443	1.4097		

31-Ni	0.7501	0.7757	-0.0101	-0.0057	1.4097		
32-Ni	-0.0188	0.1050	-0.0101	0.8443	0.0643		
33-Ni	-0.0115	-0.0046	0.0944	-0.0057	0.0643		
34-Ni	0.7598	0.1363	1.5212	-0.0057	1.4592		
35-Ni	-0.0203	-0.0046	0.8441	-0.0057	0.0643		
36-Ni	0.1445	1.4998	1.5212	-0.0057	1.4592		
37-Ni	0.0803	-0.0046	-0.0101	1.5397	0.0643		
38-Ni	-0.0126	1.5103	-0.0101	0.8443	1.4095		
39-Ni	0.7501	-0.0104	-0.0101	1.5397	1.4095		
40-Ni	-0.0115	0.1551	-0.0101	0.8443	0.0643		
41-Ni	0.7598	1.4998	0.8441	-0.0057	1.4592		
42-Ni	-0.0126	-0.0104	1.5212	-0.0057	1.4095		
43-Ni	0.0777	0.1111	0.0944	-0.0057	0.0999		
44-Ni	-0.0061	-0.0104	1.5212	-0.0057	1.4095		
45-Ni	-0.0203	0.1551	0.0213	0.8443	0.0643		
46-Ni	0.7501	-0.0104	0.7998	1.5397	1.4095		
47-Ni	-0.0061	1.5103	0.7998	0.8443	1.4095		
48-Ni	0.1070	-0.0046	0.0213	1.5397	0.0643		

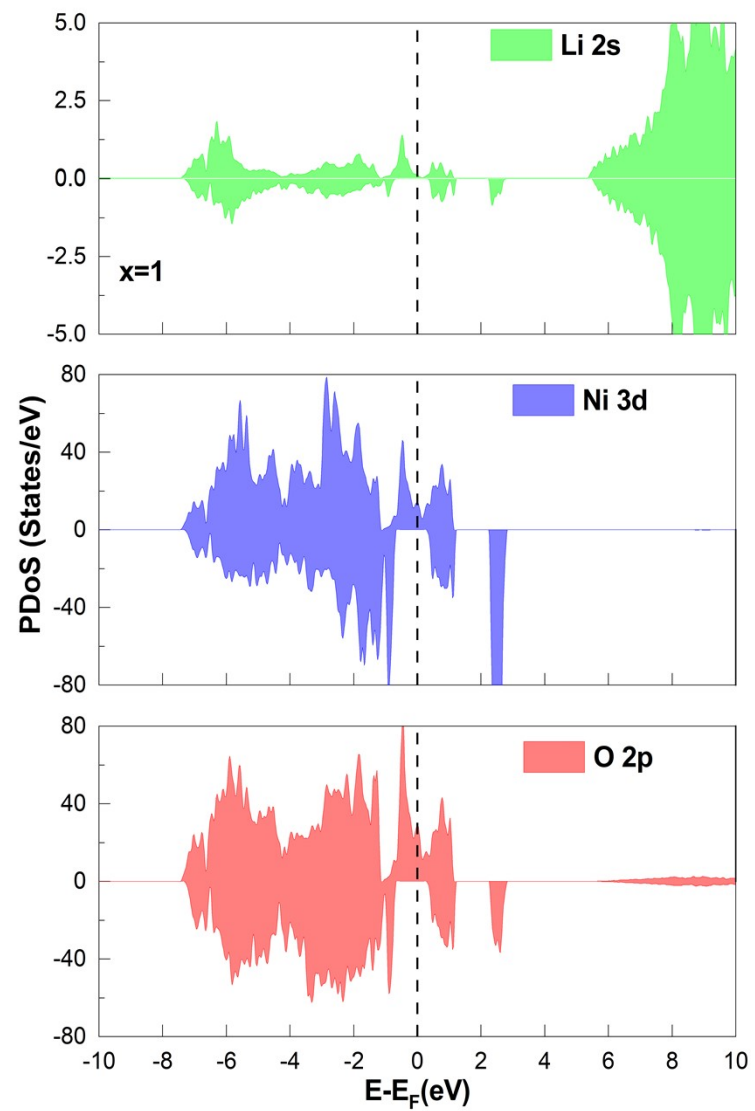


Fig.S1 Partial density of states in Li_xNiO_2 at $x=1$, with contribution from Li (2s), Ni (3d) and O (2p) atomic orbitals along the Fermi level (E_F).

Table S2. Position of Lithium vacancies in three A, B, C layers of LNO, where under the heads A, B, C are positions of first Li ion in the layer. The numerals denote the Li is taken away out of the 16 Li ions per layer.

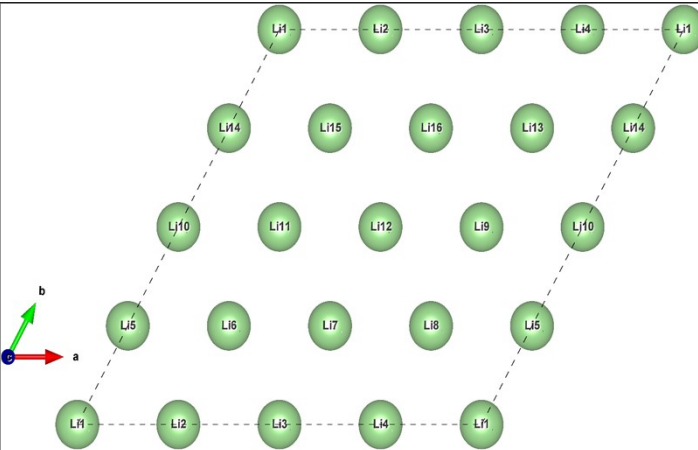
Configuration	System	A Li1 (0,0,0)	B Li1 (0.0, -1/√3)	C Li1 (0.0, 1/√3)	 <p>The single plane of Li, where indexing is done to represent the position of Li-vacancy created from that position.</p>
8c (Most stable)	Li _{0.25} NiO ₂	2,4,5,6,7,8,9,11,13,14,15,16	2,4,5,6,7,8,9,11,13,14,15,16	2,4,5,6,7,8,9,11,13,14,15,16	
8a (Least stable)	Li _{0.25} NiO ₂	1,2,3,4,5,8,9,10,13,14,15,16	1,2,3,4,5,8,9,10,13,14,15,16	1,2,3,4,5,8,9,10,13,14,15,16	
7c (Most stable)	Li _{0.5} NiO ₂	2,4,6,8,9,11,13,15	2,4,6,8,9,11,13,15	2,4,6,8,9,11,13,15	
7a (Least stable)	Li _{0.5} NiO ₂		1,2,3,5,6,7,10,11,12,14,15,16	2,3,4,6,7,8,9,11,12,13,15,16	
6c (Most stable)	Li _{0.66} NiO ₂		2,4,6,8,9,11,13,15	1,3,5,7,10,12,14,16	
6b (Least stable)	Li _{0.66} NiO ₂		1,2,3,4,5,6,7,8	9,10,11,12,13,14,15,16	
5a (Most stable)	Li _{0.75} NiO ₂	9,10,11,12	5,6,7,8	1,2,3,4	
5d (Least stable)	Li _{0.75} NiO ₂		1,2,3,10,11,12	1,2,3,10,11,12	

Table S3. Optimized values of the structural parameters in fully lithiated and delithiated LiNiO₂. Single layer structures are listed first, followed by the multilayer structures. The mixing energy is calculated using Equation 1 in the main manuscript.

Structure	System	Lattice parameters (Å)			Mixing Energy (E _{Mixing})	
		a	b	c	eV/per atom	
	LiNiO ₂ (relax)	11.5814	11.5814	14.2595		
	LiNiO ₂	11.5046	11.5046	14.0157		
Single layer	1b	Li _{0.916} NiO ₂	11.5029	11.5029	14.0521	-0.00038
	1c	Li _{0.916} NiO ₂	11.4636	11.4636	14.0396	-0.00779
	3a	Li _{0.833} NiO ₂	11.4722	11.4722	14.0469	-0.00471
	3b	Li _{0.833} NiO ₂	11.4165	11.4165	14.0845	-0.00315
	4a	Li _{0.75} NiO ₂	11.3870	11.3870	13.9967	0.009521
	4b	Li _{0.75} NiO ₂	11.4229	11.4229	14.0223	0.008959

Multilayer		$\text{Li}_{0.916}\text{NiO}_2$	11.4761	11.4761	14.0542	-0.00775
		$\text{Li}_{0.916}\text{NiO}_2$	11.4843	11.4686	14.0552	-0.00753
		$\text{Li}_{0.833}\text{NiO}_2$	11.4776	11.4776	14.0991	-0.00728
		$\text{Li}_{0.833}\text{NiO}_2$	11.4788	11.4655	14.0693	-0.01083
	5a	$\text{Li}_{0.75}\text{NiO}_2$	11.4254	11.4467	14.0831	-0.01968
	5d	$\text{Li}_{0.75}\text{NiO}_2$	11.3983	11.4496	14.0801	-0.00925
	6b	$\text{Li}_{0.667}\text{NiO}_2$	11.4096	11.3779	14.1016	0.005455
	6c	$\text{Li}_{0.667}\text{NiO}_2$	11.4042	11.4042	14.0953	-0.00946
		$\text{Li}_{0.58}\text{NiO}_2$	11.3866	11.3866	14.1506	-0.00854
		$\text{Li}_{0.58}\text{NiO}_2$	11.3793	11.3793	14.1387	-0.01525
	7a	$\text{Li}_{0.5}\text{NiO}_2$	11.3459	11.3985	13.9743	0.009452
	7c	$\text{Li}_{0.5}\text{NiO}_2$	11.3304	11.3779	14.1370	-0.01667
		$\text{Li}_{0.41}\text{NiO}_2$	11.3186	11.3335	14.1609	-0.01619
		$\text{Li}_{0.41}\text{NiO}_2$	11.3454	11.2758	14.1639	-0.01339
		$\text{Li}_{0.33}\text{NiO}_2$	11.3843	11.2706	14.0401	-0.0017
		$\text{Li}_{0.33}\text{NiO}_2$	11.2809	11.3240	14.1175	-0.00947
	8a	$\text{Li}_{0.25}\text{NiO}_2$	11.2873	11.2873	13.9924	0.000836
	8c	$\text{Li}_{0.25}\text{NiO}_2$	11.2965	11.2965	14.1184	-0.01572
		$\text{Li}_{0.167}\text{NiO}_2$	11.2666	11.2666	13.9581	0.001363
		$\text{Li}_{0.167}\text{NiO}_2$	11.2846	11.2520	14.0254	-0.01025
	$\text{Li}_{0.083}\text{NiO}_2$	11.2538	11.2538	13.8524	0.001689	
	$\text{Li}_{0.083}\text{NiO}_2$	11.2687	11.2275;	13.9108	-0.00339	
		12 Atom LNO	2.8953	2.8953	14.2595	
		48 Atom LNO	5.7366	5.7366	14.0592	
		NiO_2	11.2308	11.2308	13.7727	
		Li	3.4274	3.4274	3.4274	

Table. S4. Calculated magnetic moments of Ni, Mn in $\text{Li}_x\text{Ni}_y\text{Mn}_{1-y}\text{O}_2$.

S. No.	$\text{Li}_x\text{Ni}_{0.875}\text{Mn}_{0.125}\text{O}_2$				S. No.	$\text{Li}_x\text{Ni}_{0.75}\text{Mn}_{0.25}\text{O}_2$					S. No.	$\text{Li}_x\text{Ni}_{0.625}\text{Mn}_{0.375}\text{O}_2$			
	x=1	x=0.25	x=0.5	x=0.75		x=1	x=0.25	x=0.5	x=0.75 (chain)	x=0.75 (square)		x=1	x=0.25	x=0.5	x=0.75
	μ_B	μ_B	μ_B	μ_B		μ_B	μ_B	μ_B	μ_B	μ_B		μ_B	μ_B	μ_B	μ_B
1-Ni	1.5402	0.0292	0.8388	1.5	1-Mn	2.6847	2.6098	2.6397	2.6456	2.6685	1-Mn	2.6571	2.6303	2.6457	2.6464
2-Ni	0.0575	0.0049	-0.0113	0.0859	2-Ni	0.8597	0.0107	0.0503	0.8846	1.5515	2-Ni	1.5321	0.0525	0.8631	1.5268
3-Ni	1.5356	0.0122	0.1328	1.5189	3-Mn	2.6847	2.6254	2.6441	2.6456	2.6685	3-Mn	2.6562	2.6300	2.6448	2.6470
4-Mn	2.6663	2.6517	2.6502	2.6619	4-Ni	0.8597	0.0102	0.0524	0.8846	1.5515	4-Ni	1.5351	0.0566	0.8227	1.5274
5-Ni	1.5294	0.8478	0.8021	0.0161	5-Ni	0.8597	-0.8584	-0.7705	-0.8164	0.0294	5-Mn	2.6812	2.7047	2.6765	2.6668
6-Ni	0.8204	-0.0076	0.7673	0.7597	6-Ni	1.5582	0.0115	-0.7911	-0.8347	0.8754	6-Ni	1.5539	0.0964	1.4637	0.8389
7-Ni	0.8736	0.8932	0.7985	0.0294	7-Ni	0.8597	-0.8482	-0.7731	-0.8164	0.0294	7-Mn	2.6847	2.7058	2.6745	2.6666
8-Mn	2.6656	2.6502	2.6751	2.6304	8-Ni	1.5582	-0.0034	-0.7916	-0.8346	0.8754	8-Ni	1.5549	0.0958	0.9244	0.8390
9-Ni	1.5268	0.0180	0.0122	1.5182	9-Ni	0.8597	-0.0353	0.0503	0.8779	1.5515	9-Ni	0.9380	0.0553	0.2465	0.9477
10-Ni	0.0616	-0.0078	0.0504	0.1557	10-Mn	2.6847	-2.6273	2.6441	2.6426	2.6685	10-Mn	2.6485	2.6282	2.6352	2.6409
11-Ni	0.8558	-0.0005	-0.0184	0.8499	11-Ni	0.8597	-0.0469	0.0524	0.8779	1.5515	11-Ni	0.9400	0.0594	0.8909	0.9471
12-Ni	1.5393	0.0137	1.4682	1.5226	12-Mn	2.6847	-2.6285	2.6397	2.6426	2.6685	12-Mn	2.6505	2.6284	2.6419	2.6398
13-Ni	1.5286	0.0179	0.7892	0.8243	13-Ni	1.5582	0.0120	-0.7912	1.3860	0.8754	13-Ni	0.8890	0.0332	0.1150	0.8379
14-Ni	0.8696	0.8632	0.7873	0.8134	14-Ni	0.8597	-0.8527	-0.7731	-0.0301	0.0294	14-Ni	1.5422	1.5516	0.8287	0.8223
15-Ni	0.0947	-0.0063	0.0255	0.0503	15-Ni	1.5582	0.0012	-0.7915	1.3856	0.8754	15-Ni	0.9055	0.0332	0.1296	0.8375

16-Ni	0.0260	0.8385	0.0908	0.0239	16-Ni	0.8597	-0.8567	-0.7705	-0.0301	0.0294	16-Ni	1.5435	1.5516	0.8428	0.8217
17-Ni	0.8204	0.0515	0.7673	0.8280	17-Ni	0.8597	-0.0094	0.0592	0.8276	0.0294	17-Ni	0.9026	0.8345	0.1221	0.8883
18-Ni	0.0616	-0.0236	0.0504	0.0981	18-Ni	0.8597	0.0092	-0.7977	0.8445	1.5514	18-Ni	1.5443	0.0331	0.8226	1.5477
19-Ni	1.5286	0.7791	0.7892	1.5350	19-Ni	0.8597	-0.8092	0.0560	0.8276	0.0294	19-Ni	0.8879	0.8330	0.1171	0.8860
20-Ni	1.5356	0.0068	0.1328	0.8599	20-Ni	0.8597	-0.0048	-0.7943	0.8455	1.5514	20-Ni	1.5470	0.0345	0.8368	1.5469
21-Ni	0.8558	-0.0055	-0.0184	0.7812	21-Ni	1.5582	0.0822	-0.8085	0.8455	0.8754	21-Ni	0.9446	0.0618	0.8977	0.8553
22-Ni	0.8696	0.8131	0.7873	0.8188	22-Mn	2.6848	2.6420	2.6285	2.6035	2.6688	22-Mn	2.6484	2.6593	2.6364	2.6225
23-Mn	2.6663	2.6479	2.6502	2.6218	23-Ni	1.5581	0.0732	-0.8031	0.8455	0.8754	23-Ni	0.9362	0.0619	0.2636	0.8537
24-Ni	0.8737	0.8278	0.7985	0.8324	24-Mn	2.6848	2.6324	2.6282	2.6035	2.6688	24-Mn	2.6521	2.6565	2.6426	2.6227
25-Ni	1.5393	0.0181	1.4683	1.5329	25-Ni	0.8597	0.0117	-0.7977	0.8358	1.5514	25-Mn	2.6838	2.6505	2.6766	2.6757
26-Ni	0.0947	0.0078	0.0255	0.0664	26-Ni	0.8597	-0.7980	0.0561	0.8291	0.0294	26-Ni	1.5526	0.8965	1.4591	1.5488
27-Ni	1.5403	0.0360	0.8387	1.5286	27-Ni	0.8597	0.0099	-0.7943	0.8358	1.5514	27-Mn	2.6811	2.6484	2.6747	2.6746
28-Mn	2.6656	2.6787	2.6750	2.6515	28-Ni	0.8597	-0.8249	0.0592	0.8291	0.0294	28-Ni	1.5518	0.8501	0.9324	1.5468
29-Ni	0.0260	0.1290	0.0908	-0.0002	29-Mn	2.6848	-2.6461	2.6282	2.6083	2.6688	29-Mn	2.6566	2.6565	2.6422	2.6372
30-Ni	0.0575	0.0008	-0.0113	0.0057	30-Ni	1.5581	0.7140	-0.8034	-0.8414	0.8754	30-Ni	1.5357	0.0548	0.8631	0.0605
31-Ni	1.5294	0.7944	0.8021	0.7898	31-Mn	2.6848	-2.6340	2.6282	2.6083	2.6688	31-Mn	2.6557	2.6565	2.6460	2.6352
32-Ni	1.5268	-0.0075	0.0122	-0.0026	32-Ni	1.5581	-0.0071	-0.8084	-0.8414	0.8754	32-Ni	1.5364	0.0547	0.8328	0.0591
33-Ni	0.8919	-0.007	-0.0033	-0.8477	33-Ni	0.8597	0.0503	-0.0432	0.8703	0.0294	33-Ni	0.9072	0.0256	0.0262	0.8678
34-Ni	0.8645	0.7923	0.8672	0.8625	34-Mn	2.6847	2.6362	2.6449	2.6364	2.6687	34-Ni	0.9675	0.1009	1.5769	0.9231
35-Ni	1.5373	-0.0080	0.0203	1.5343	35-Ni	0.8597	0.0492	-0.7756	0.8703	0.0294	35-Ni	0.8817	0.0379	0.0612	0.8594
36-Ni	0.0493	0.1222	0.8408	0.0669	36-Mn	2.6847	2.6340	2.6456	2.6364	2.6687	36-Ni	1.5307	0.7955	1.5722	1.5307
37-Ni	0.0438	0.0586	-0.0025	0.0192	37-Ni	0.8597	-0.7939	0.0207	-0.7906	1.5514	37-Ni	1.5430	0.8739	0.8358	0.8017

38-Ni	0.0493	-0.0248	0.8408	-0.0062	38-Ni	1.5582	0.0422	0.8891	-0.8266	0.8754	38-Mn	2.6464	2.6299	2.6543	2.6437
39-Ni	1.5295	0.7910	0.0143	0.7773	39-Ni	0.8597	-0.7953	0.0205	-0.7906	1.5514	39-Ni	0.9306	0.1967	0.0560	0.0577
40-Ni	1.5223	0.0074	0.8410	0.0335	40-Ni	1.5582	0.0413	1.4818	-0.8266	0.8754	40-Mn	2.6560	2.6171	2.6517	2.6432
41-Ni	1.5337	0.8252	0.8609	1.5327	41-Mn	2.6847	2.6352	2.6449	2.6377	2.6687	41-Mn	2.6856	2.6776	2.7305	2.6727
42-Ni	0.8919	-0.0043	-0.0033	-0.7951	42-Ni	0.8597	0.0516	-0.7756	0.8804	0.0294	42-Ni	1.5550	0.0867	0.8454	1.5442
43-Ni	1.5223	0.8167	0.8410	1.5147	43-Mn	2.6847	2.6327	2.6456	2.6377	2.6687	43-Mn	2.6887	2.6725	2.7187	2.6875
44-Mn	2.6627	2.6431	2.6615	2.6426	44-Ni	0.8597	0.0516	-0.0432	0.8804	0.0294	44-Ni	1.5543	0.0816	0.8942	1.5472
45-Ni	0.8645	0.0182	0.8672	0.8375	45-Ni	1.5582	0.0466	0.8890	0.8531	0.8754	45-Mn	2.6566	2.6376	2.6981	2.6194
46-Ni	0.0438	0.0203	-0.0025	0.0498	46-Ni	0.8597	-0.7938	0.0205	-0.8159	1.5514	46-Ni	1.5377	0.8305	0.2059	0.8878
47-Ni	1.5338	0.0368	0.8609	0.8530	47-Ni	1.5582	0.0510	1.4821	0.8531	0.8754	47-Mn	2.6567	2.6438	2.6775	2.6189
48-Mn	2.6684	2.6787	2.6578	2.6193	48-Ni	0.8597	-0.7952	0.0207	-0.8159	1.5514	48-Ni	1.5430	0.8357	0.0614	0.8841