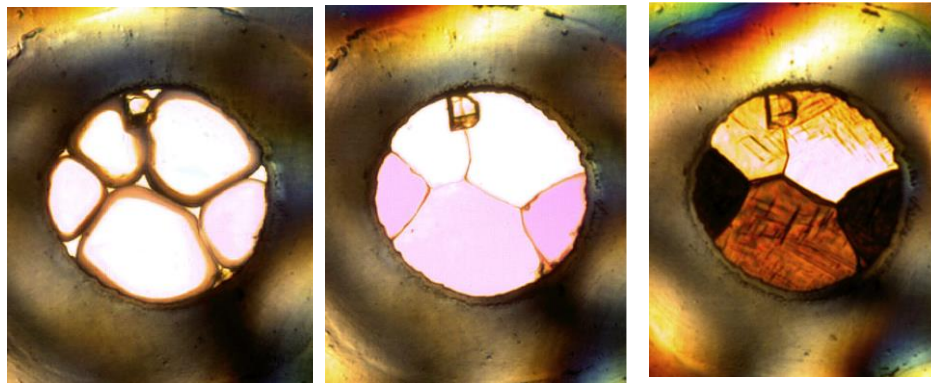


High Pressure: Making it, Measuring it, and Avoiding Pitfalls

Stefan Klotz

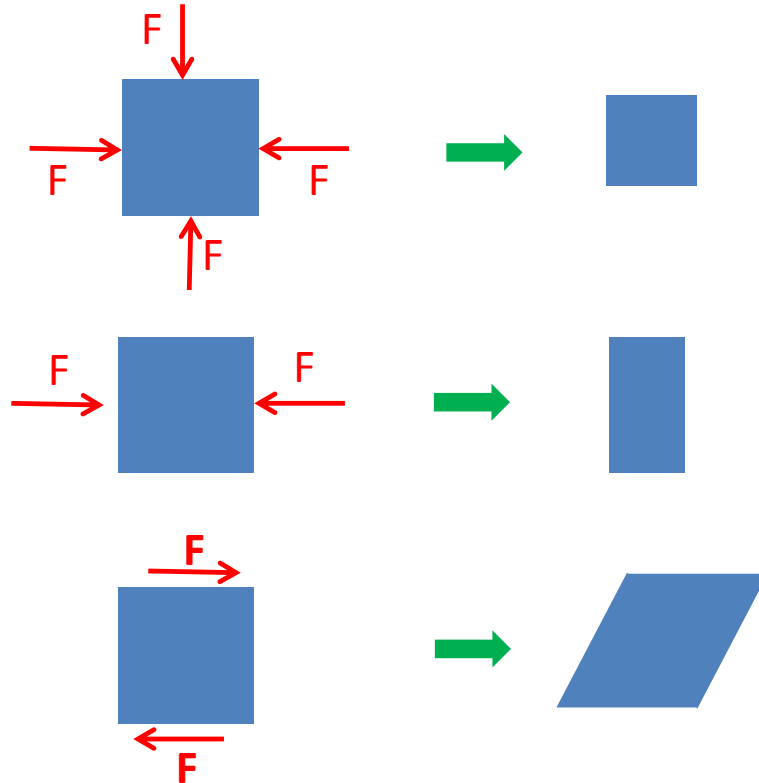
Sorbonne Université, Paris



K. Syassen, MPI Stuttgart

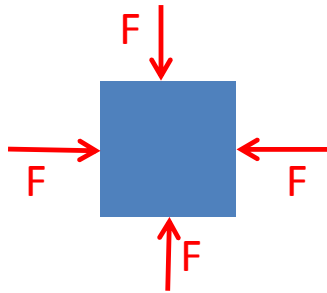
What is pressure?

« $P = \text{Force}/\text{Area}$ »



Conclusion: Pressure can't be a simple number

Pressure (« Stress ») : A rank-2 tensor



$$\sigma = \begin{pmatrix} -p & * \\ & -p \\ * & & -p \end{pmatrix}$$

$* = 0$

hydrostatic stress
(« pressure »)



$$\sigma = \begin{pmatrix} \pi & * \\ & 0 \\ * & & 0 \end{pmatrix}$$

uniaxial stress
(« pressure »)



$$\sigma = \begin{pmatrix} 0 & 0 & \pi \\ 0 & 0 & 0 \\ \pi & 0 & 0 \end{pmatrix}$$

shear stress
(« pressure »)

Remarks

1. $\sigma(\mathbf{r}) = (\sigma_{ij}(\mathbf{r}))$ → in general dependent on r !
if not: « homogeneous » pressure
2. Can always define a hydrostatic component: $p = \frac{1}{3} \cdot \text{Tr } \sigma$
3. $\sigma_{ij}(\mathbf{r}) = \sigma_{ji}(\mathbf{r})$ → only 6 components
actually only 3 (« principal stresses »)

Example



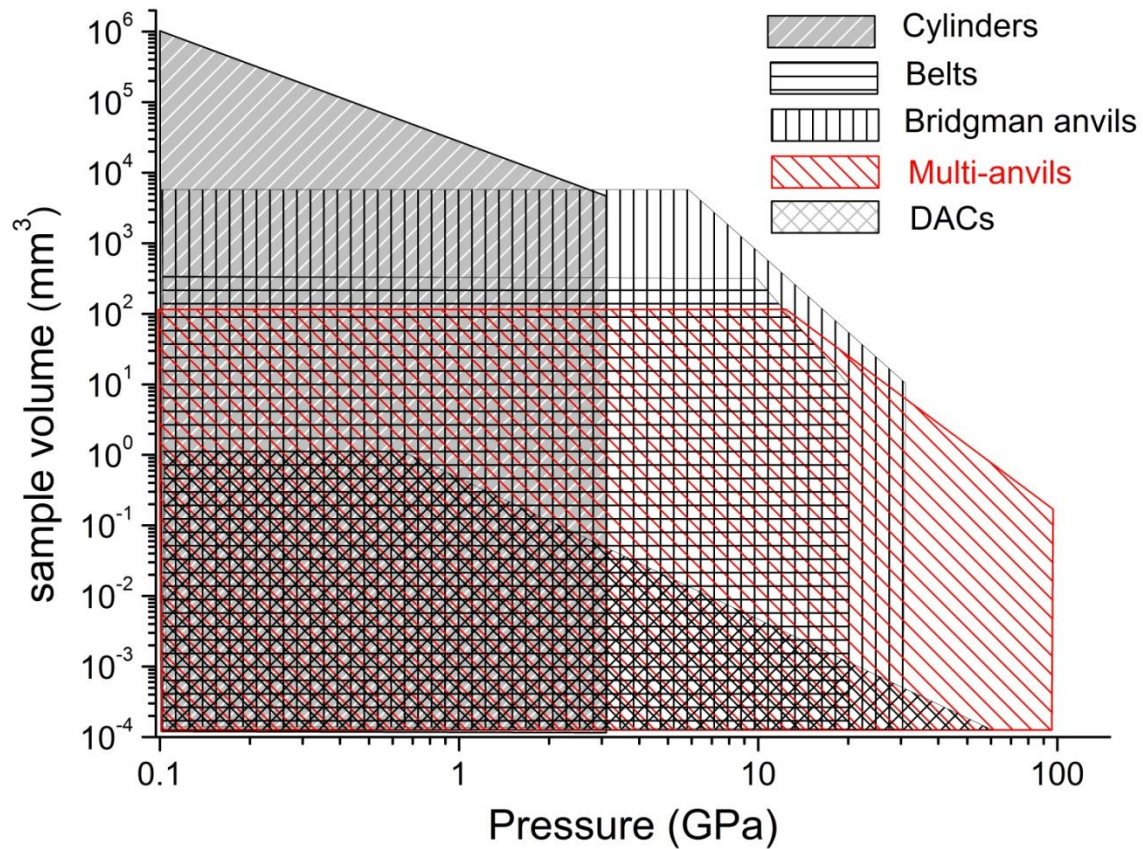
hydrostatic or non-hydrostatic?

$$\sigma = \begin{pmatrix} \pi & 0 & 0 \\ 0 & \pi & 0 \\ 0 & 0 & \pi \end{pmatrix}$$

$$\pi = \rho g z$$

→ Hydrostatic but not homogeneous

Making pressure



The cylinder

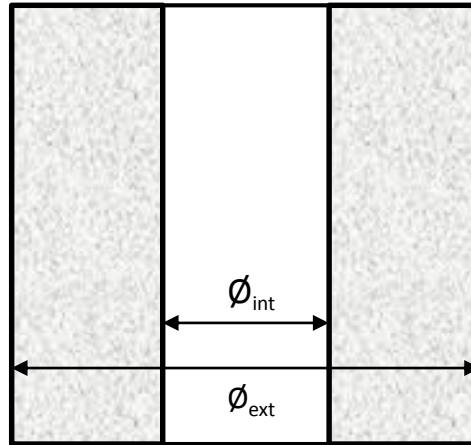
The most common high pressure device

- Pipes
- Car engines
- Hydraulic systems
- High pressure gas bottles
- Pressure cookers
- Autoclaves (= high P/T vessels for synthesis)
- Food processing

- High pressure research equipment

Pressure limit: Useful facts

'monobloc'



$K = \phi_{ext} / \phi_{int}$ 'wall ratio'
 σ_Y : yield strength

Onset of plasticity:

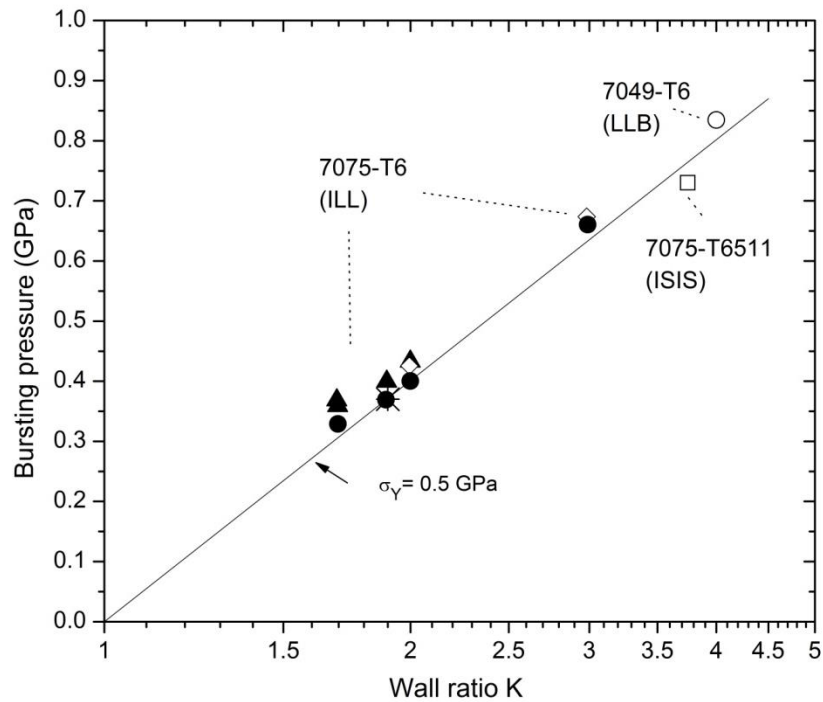
$$P = \sigma_Y \frac{(K^2 - 1)}{\sqrt{3} K^2}$$

Burst pressure:

$$P = \frac{2\sigma_Y}{\sqrt{3}} \ln K$$

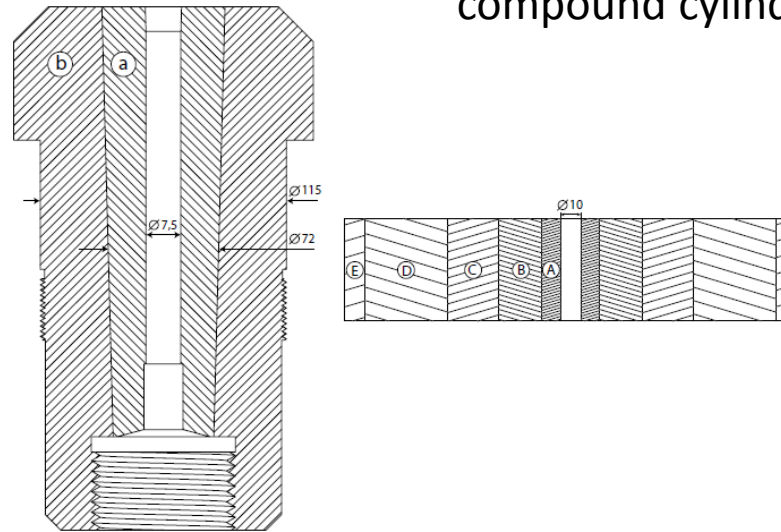
Burst pressure

$$P = \frac{2\sigma_Y}{\sqrt{3}} \ln K$$



Frettage

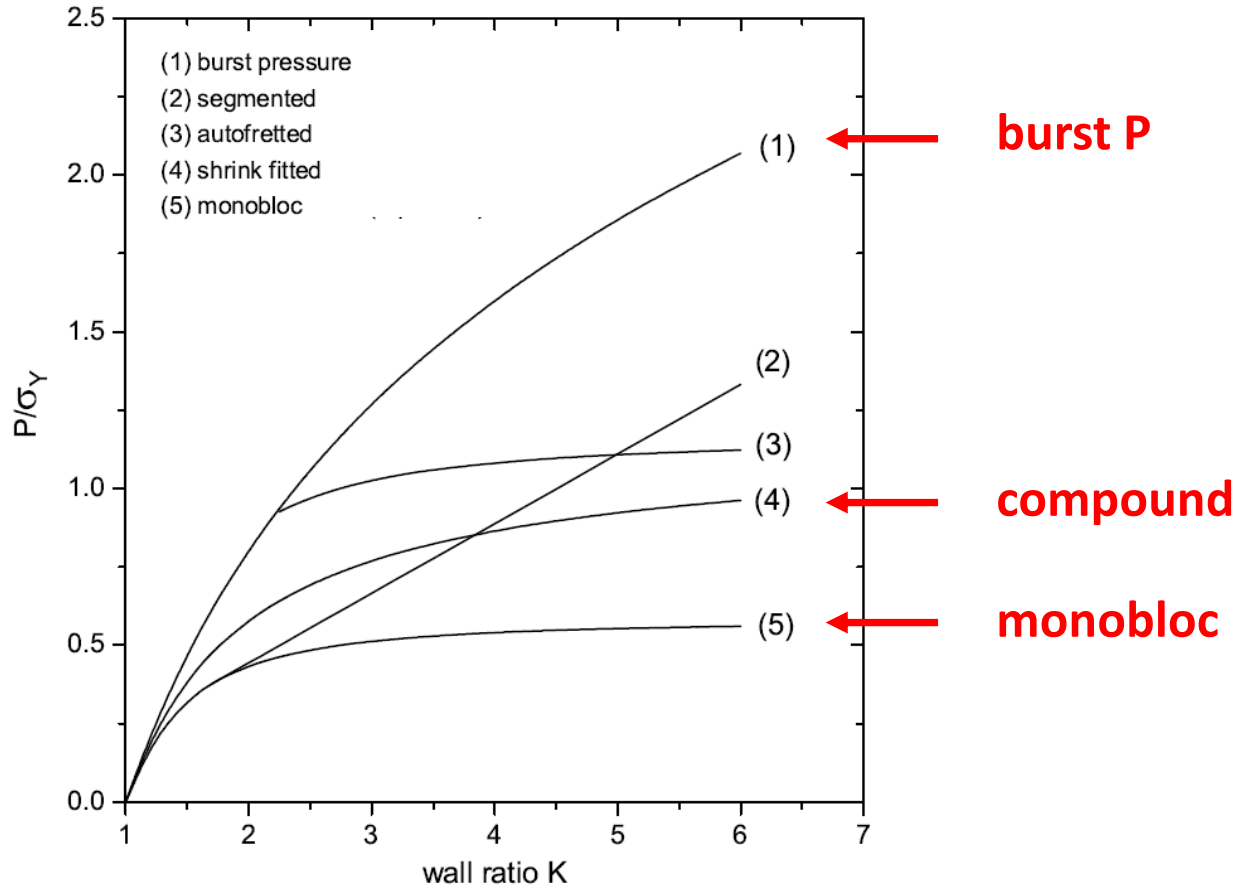
'compound cylinder'



$$P = \frac{2\sigma_Y}{\sqrt{3}} \frac{K - 1}{K}$$

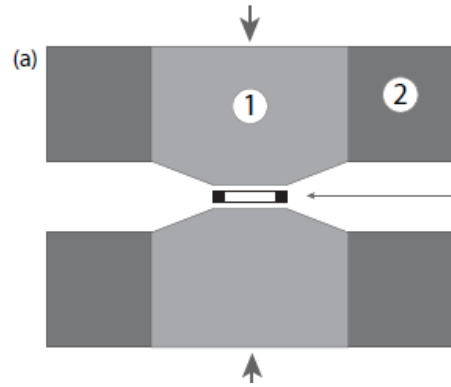
Monobloc:
$$P = \sigma_Y \frac{(K^2 - 1)}{\sqrt{3} K^2}$$

Cylinder: summary



Making pressure: Bridgman anvils

(flat, profiled, toroidal)



Making pressure: The Paris-Edinburgh cell/press

« Compact high-capacity press for HP research applications»



Compact: 10-100 kg
High capacity: 50-450 tonnes
Research: P=1-40 GPa

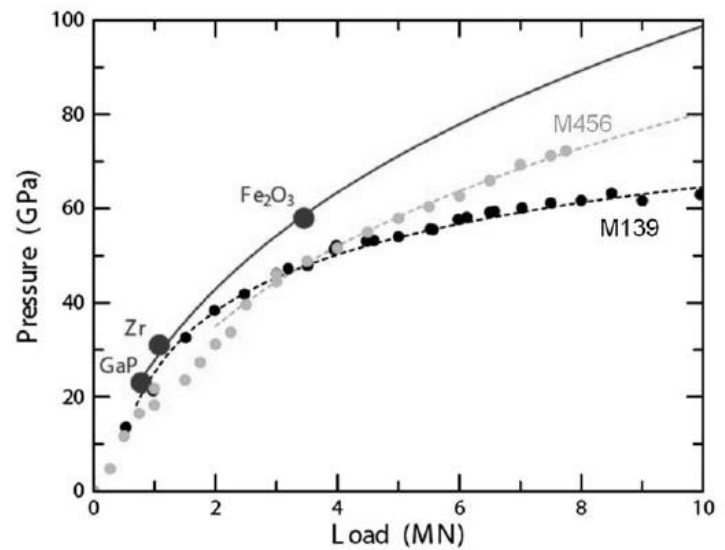
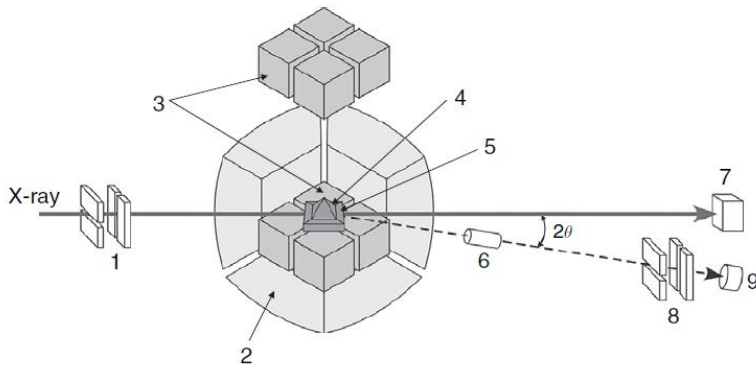
Making pressure: Multianvil cells



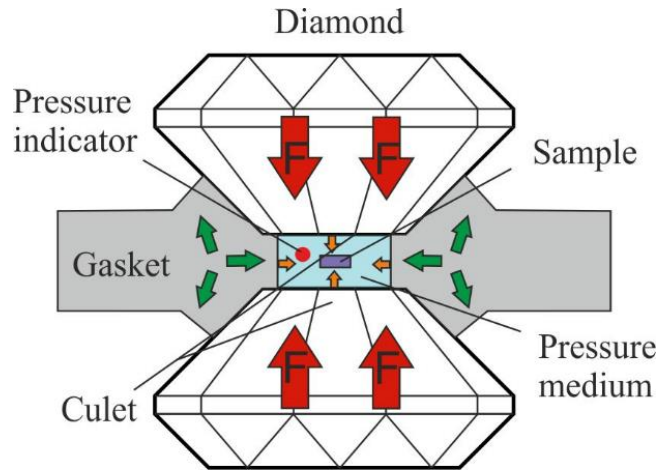
ID06 ESRF, typical: 20 GPa/2000K



E. Ito, Misasa



Making pressure: The diamond anvil cell (DAC)



See:
50% of all talks of this School!



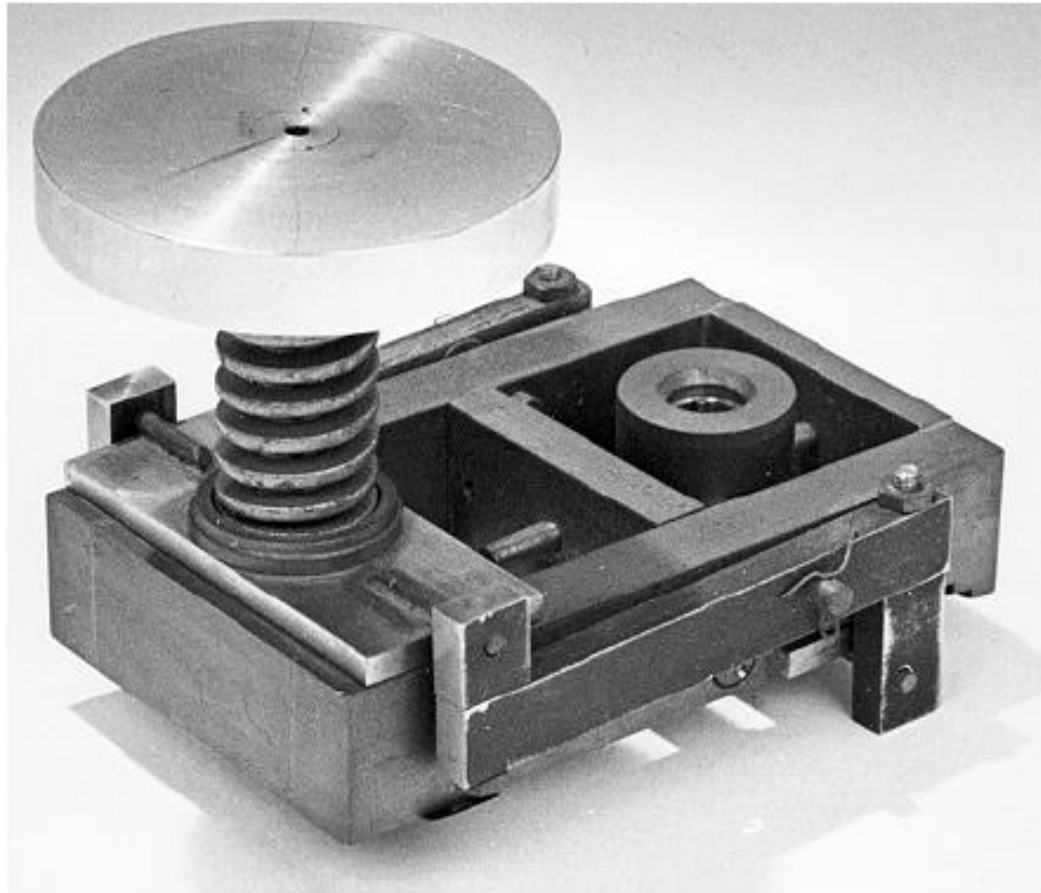
Fig. 2. Charles Weir, ca. 1960.



Fig. 3. A. Van Valkenburg, 1962.

NBS Laboratories, Washington, 1958

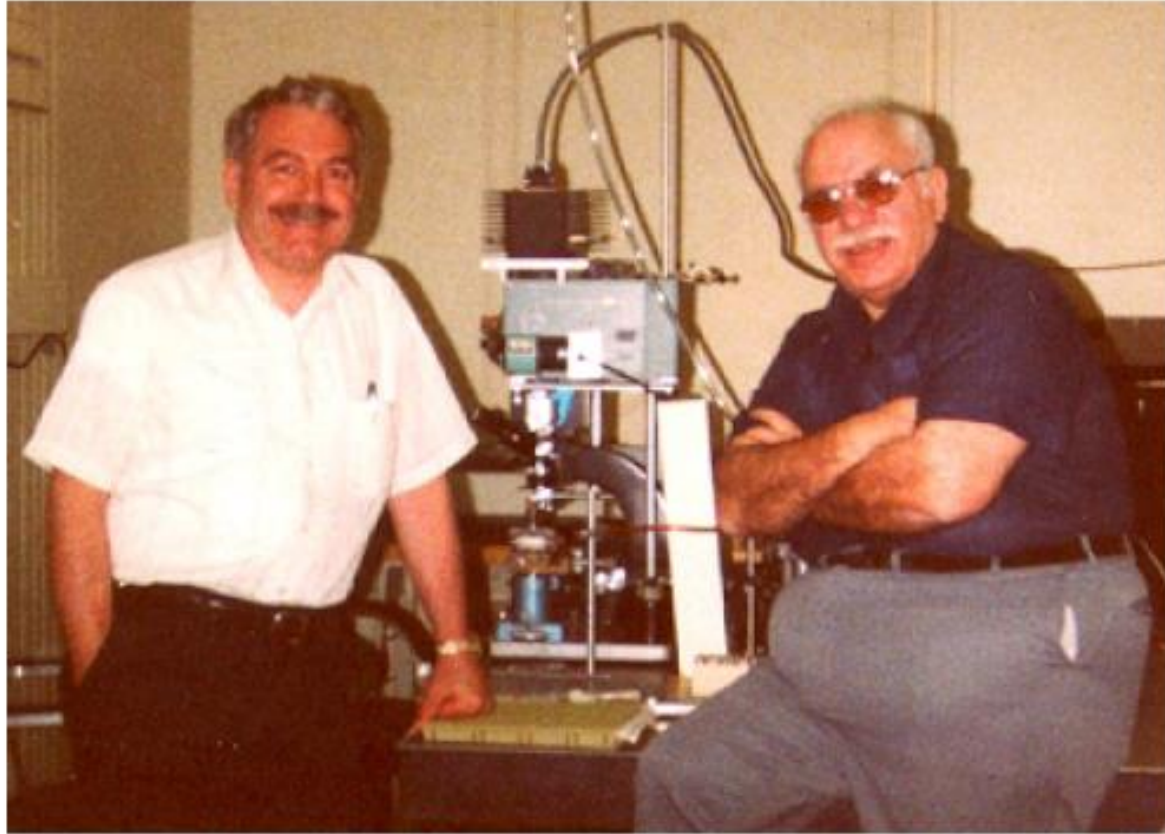
Overview: W. Basset, HPR 29, 163 (2009)



« ...Charles E. Weir fabricated it utilizing only a lathe, drill press, hack saw, soldering gun, threading tools, files, and a high speed grinding wheel to polish the culets... »

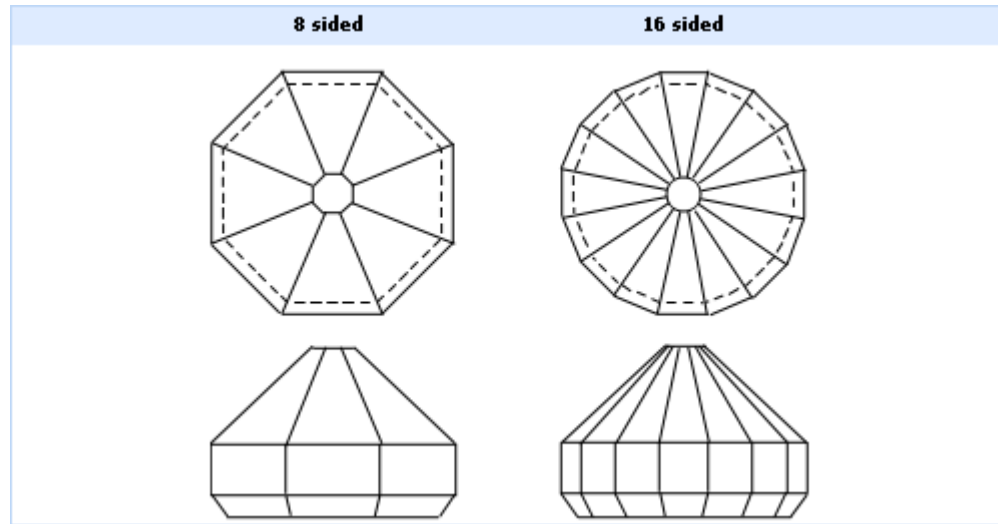
(G. Piermarini & S. Block)

1972: The ruby pressure gauge



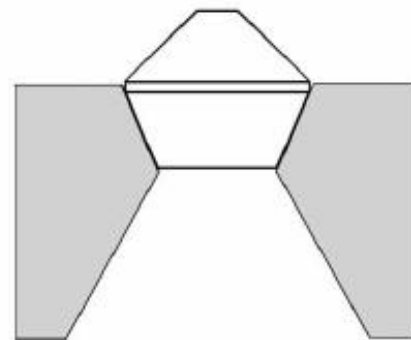
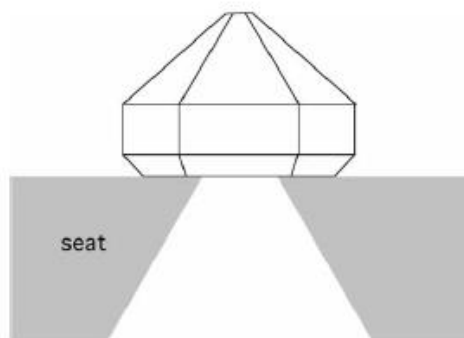
G. Piermarini & S. Block, ca. 1984

What makes a DAC:



1. Diamonds

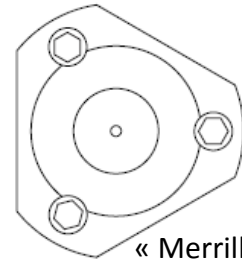
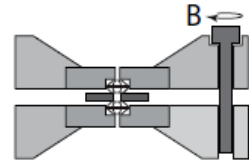
(see following talk
Hantsetters)



1. Seats

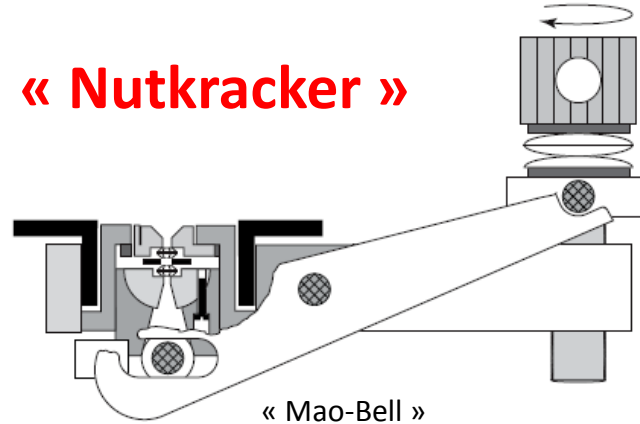
3. Load frames

Screws

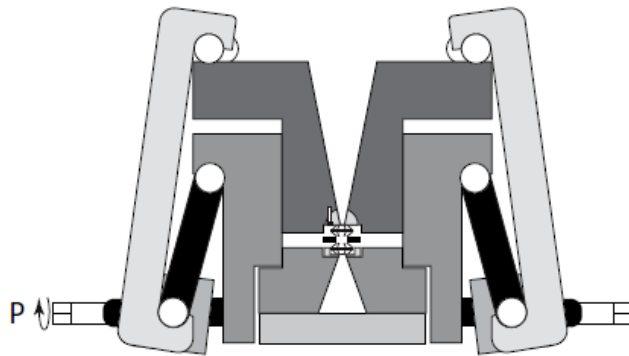


« Merrill-Bassett »

« Nutcracker »

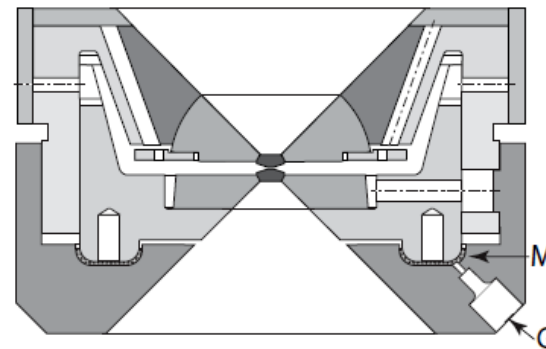


Toggle-latch



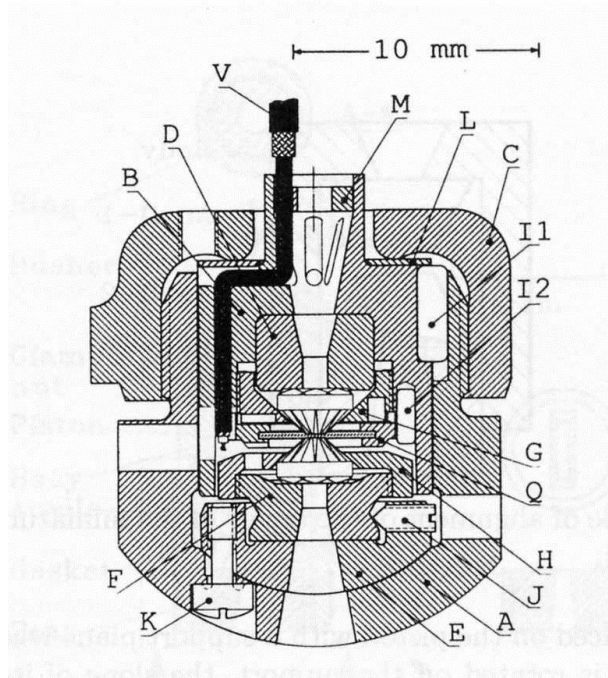
« Syassen-Holzapfel »

Membrane

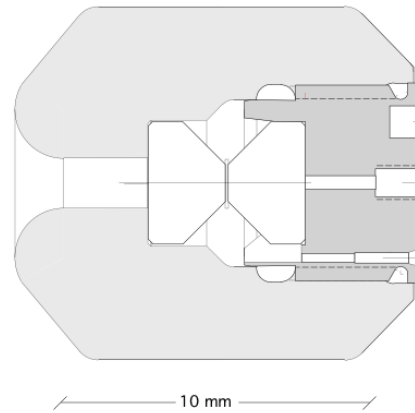


Miniature DACs

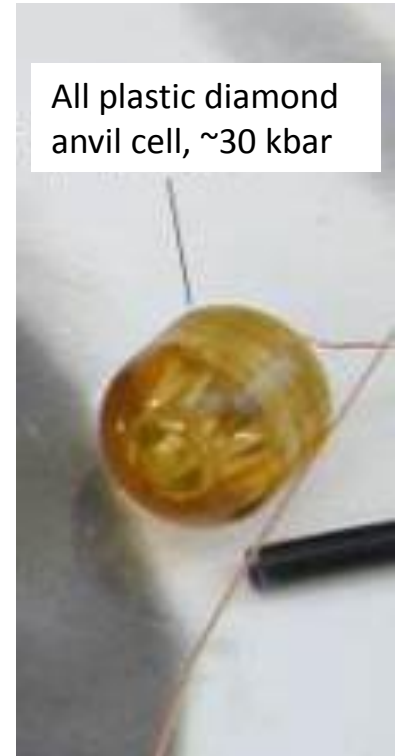
for high magnetic fields



S. Tozer et al.
RSI 64, 2607 (1993)



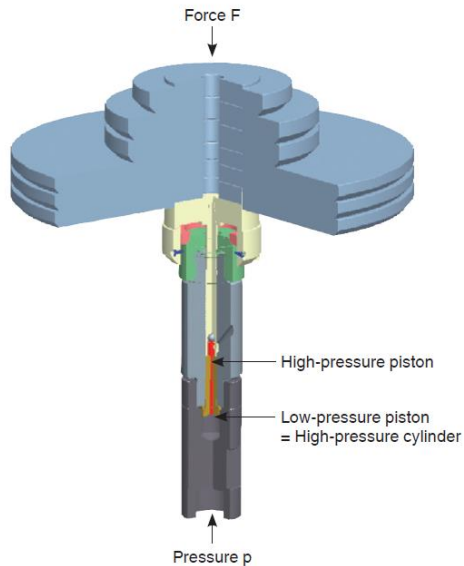
D.E. Graf
HPR 2011



Measuring pressure

Primary pressure scales:
(→use only the definition of pressure)

$$P = F/A$$



High pressure balances

P-range: 0-5 kbar
Accuracy: 0.02%

High pressure balances to 3 GPa

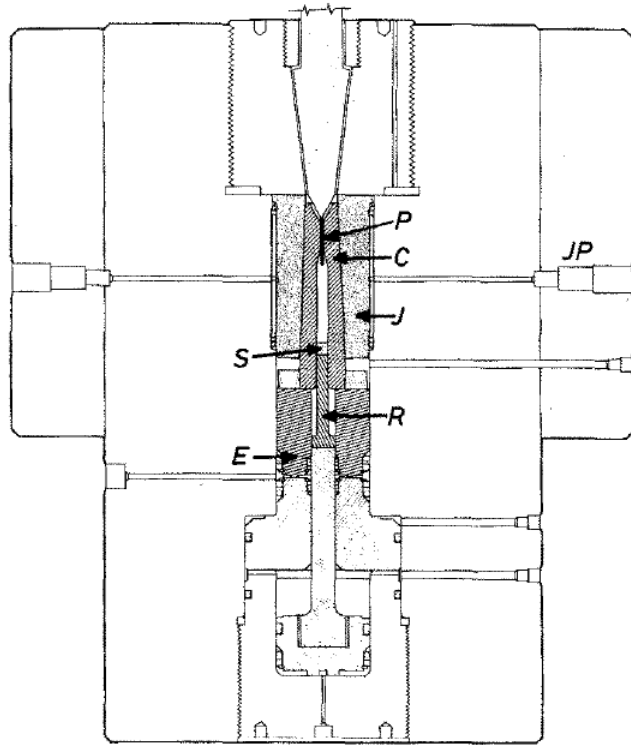


FIG. 1. 26-kbar piston gauge, schematic: P, carboloy gauge piston; C, cylinder, J, jacket; JP, connection for jacket pressure; S, seal; R, pressure generator ram; E, end load ram.

- Technically difficult
- Not commercially available
- High exploitation costs

Accuracy: ~ 0.1%

Secondary pressure scales

= Methods which:

- Are more adapted to a specific P range and device
- Have been calibrated to a primary standard
 - Volume scales: $V=V(P)$
 - Optical scales: $\lambda=\lambda(P)$

The Decker NaCl scale (1971)

TABLE II. Calculated pressure at selected temperatures and compressions, $\Delta\gamma/\gamma_0$ or $\Delta V/V_0$, for NaCl.

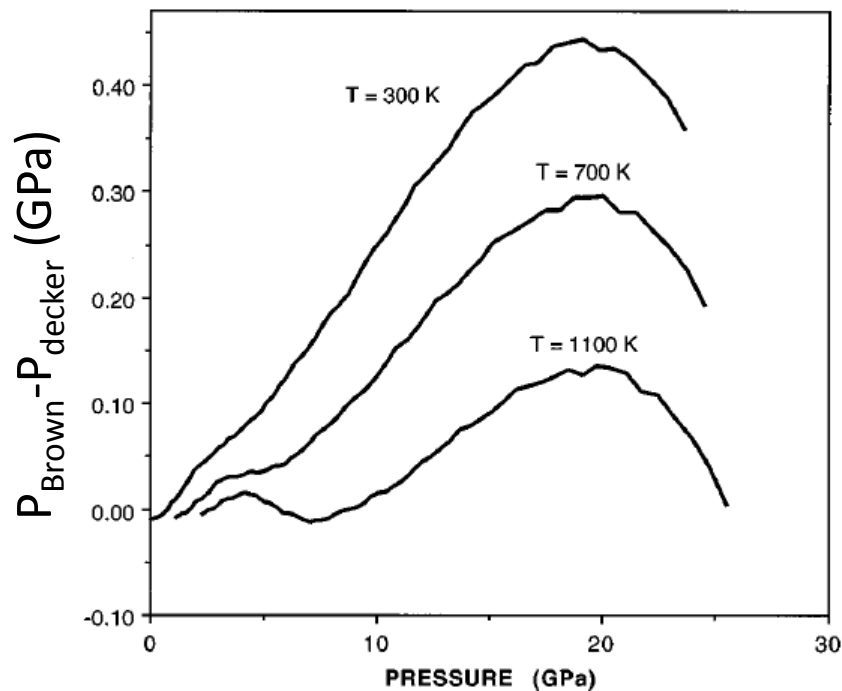
$\Delta V/V_0$	0°	25° C	100° C	200° C	300° C	500° C	800° C	$\Delta\gamma/\gamma_0$	$\Delta V/V_0$	0°	25° C	100° C	200° C	300° C	500° C	800° C	$\Delta\gamma/\gamma_0$
0.0		0.00	2.13	5.00	7.89	13.72	22.48	0.0	-0.1956	87.17	87.85	89.95	92.81	95.71	101.58	110.44	-0.070
-0.0060	0.74	1.44	3.57	6.44	9.34	15.16	23.93	-0.002	-0.2008	91.21	91.89	93.98	96.84	99.75	105.61	114.48	-0.072
-0.0120	2.24	2.94	5.06	7.93	10.83	16.65	25.43	-0.004	-0.2060	95.36	96.04	98.13	100.99	103.90	109.76	118.64	-0.074
-0.0179	3.77	4.47	6.60	9.47	12.37	18.19	26.97	-0.006	-0.2111	99.63	100.31	102.40	105.26	108.16	114.03	122.91	-0.076
-0.0238	5.36	6.06	8.18	11.06	13.95	19.78	28.56	-0.008	-0.2162	104.01	104.69	106.79	109.64	112.55	118.42	127.30	-0.078
-0.0297	7.00	7.70	9.82	12.69	15.59	21.42	30.20	-0.010	-0.2213	108.53	109.21	111.30	114.15	117.06	122.93	131.81	-0.080
-0.0356	8.68	9.38	11.51	14.38	17.28	23.11	31.89	-0.012	-0.2264	113.17	113.84	115.93	118.79	121.69	127.57	136.45	-0.082
-0.0414	10.42	11.12	13.24	16.12	19.01	24.85	33.63	-0.014	-0.2314	117.94	118.61	120.70	123.56	126.46	132.33	141.22	-0.084
-0.0472	12.22	12.91	15.04	17.91	20.81	26.64	35.43	-0.016	-0.2364	122.84	123.52	125.60	128.46	131.36	137.23	146.12	-0.086
-0.0530	14.07	14.76	16.88	19.76	22.65	28.49	37.28	-0.018	-0.2414	127.88	128.55	130.64	133.49	136.40	142.27	151.16	-0.088
-0.0588	15.97	16.67	18.79	21.66	24.56	30.40	39.19	-0.020	-0.2464	133.06	133.73	135.82	138.67	141.57	147.45	156.34	-0.090
-0.0646	17.93	18.63	20.75	23.62	26.52	32.36	41.16	-0.022	-0.2514	138.38	139.06	141.14	143.99	146.89	152.77	161.67	-0.092
-0.0703	19.96	20.65	22.77	25.65	28.54	34.38	43.19	-0.024	-0.2563	143.86	144.53	146.61	149.46	152.36	158.24	167.14	-0.094
-0.0760	22.04	22.74	24.86	27.73	30.63	36.47	45.27	-0.026	-0.2612	149.49	150.15	152.23	155.08	157.98	163.86	172.76	-0.096
-0.0817	24.19	24.88	27.00	29.87	32.77	38.61	47.42	-0.028	-0.2661	155.26	155.93	158.01	160.86	163.76	169.64	178.54	-0.098
-0.0873	26.40	27.10	29.21	32.08	34.98	40.83	49.64	-0.030	-0.2710	161.20	161.87	163.94	166.79	169.70	175.58	184.48	-0.100
-0.0930	28.68	29.37	31.49	34.36	37.26	43.11	51.92	-0.032	-0.2998	200.44	201.11	203.17	206.02	208.92	214.80	223.72	-0.112
-0.0986	31.03	31.72	33.84	36.71	39.61	45.45	54.27	-0.034	-0.3045	207.63	208.29	210.35	213.20	216.10	221.98	230.91	-0.114
-0.1042	33.44	34.13	36.25	39.12	42.02	47.87	56.69	-0.036	-0.3092	215.01	215.67	217.73	220.57	223.47	229.36	238.29	-0.116
-0.1097	35.93	36.62	38.74	41.61	44.51	50.35	59.18	-0.038	-0.3139	222.99	223.26	225.31	228.15	231.05	236.94	245.87	-0.118
-0.1153	38.49	39.18	41.30	44.16	47.07	52.92	61.74	-0.040	-0.3185	230.38	231.05	233.10	235.94	238.84	244.73	253.66	-0.120
-0.1208	41.13	41.82	43.93	46.80	49.70	55.55	64.38	-0.042	-0.3232	238.39	239.05	241.10	243.94	246.84	252.73	261.66	-0.122
-0.1263	43.84	44.53	46.64	49.51	52.41	58.26	67.10	-0.044	-0.3278	246.61	247.27	249.32	252.16	255.06	260.95	269.88	-0.124
-0.1317	46.63	47.32	49.43	52.30	55.20	61.06	69.89	-0.046	-0.3324	255.06	255.72	257.77	260.60	263.50	269.39	· · ·	-0.126
-0.1372	49.51	50.20	52.31	55.18	58.08	63.93	72.77	-0.048	-0.3369	263.74	264.39	266.44	269.28	272.17	278.06	· · ·	-0.128
-0.1426	52.47	53.16	55.26	58.13	61.03	66.89	75.73	-0.050	-0.3415	272.65	273.31	275.35	278.19	281.08	286.97	· · ·	-0.130
-0.1480	55.51	56.20	58.31	61.17	64.06	69.93	78.77	-0.052	-0.3460	281.81	282.46	284.51	287.34	290.23	296.12	· · ·	-0.132
-0.1534	58.64	59.33	61.44	64.30	67.21	73.06	81.91	-0.054	-0.3505	291.21	291.87	293.91	296.74	299.63	· · ·	· · ·	-0.134
-0.1588	61.87	62.55	64.66	67.53	70.43	76.29	85.13	-0.056	-0.3550	300.87	301.53	303.57	306.40	309.29	· · ·	· · ·	-0.136
-0.1641	65.18	65.87	67.97	70.84	73.74	79.60	88.45	-0.058	-0.3595	310.80	311.45	313.49	316.31	· · ·	· · ·	· · ·	-0.138
-0.1694	68.59	69.28	71.38	74.25	77.15	83.01	91.86	-0.060	-0.2758	167.30	167.97	170.05	172.90	175.80	181.68	190.59	-0.102

- “Table”, semi-empirical (interatom. pot. + exp. input params)
- P-range: 0-300 kbar
- Accuracy: 0-5 % (!?)

Brown's 1999 NaCl scale

M. Brown, J. Appl. Phys. , 1999

Volume (cc/gm)	$(V_0 - V)/V_0$	300	400	500	600	700	800	900	1000	1100	1200
0.3143	0.3197	23.68	23.91	24.15	24.40	24.64	24.89	25.14	25.39	25.64	25.90
0.3166	0.3147	22.88	23.11	23.36	23.60	23.85	24.10	24.35	24.60	24.85	25.11
0.3188	0.3100	22.10	22.34	22.58	22.83	23.08	23.33	23.58	23.83	24.09	24.34
0.3211	0.3050	21.35	21.59	21.83	22.08	22.33	22.58	22.83	23.08	23.34	23.59
0.3233	0.3002	20.62	20.85	21.10	21.35	21.60	21.85	22.10	22.36	22.61	22.87
0.3256	0.2952	19.90	20.14	20.39	20.64	20.89	21.14	21.39	21.65	21.90	22.16
0.3279	0.2903	19.21	19.45	19.69	19.94	20.20	20.45	20.70	20.96	21.22	21.47
0.3301	0.2855	18.53	18.77	19.02	19.27	19.52	19.78	20.03	20.29	20.55	20.80
0.3324	0.2805	17.87	18.12	18.37	18.62	18.87	19.13	19.38	19.64	19.90	20.16
0.3347	0.2755	17.24	17.48	17.73	17.98	18.24	18.49	18.75	19.01	19.27	19.53
0.3369	0.2708	16.62	16.86	17.11	17.36	17.62	17.88	18.14	18.39	18.65	18.91
0.3392	0.2658	16.01	16.26	16.51	16.76	17.02	17.28	17.54	17.80	18.06	18.32
0.3414	0.2610	15.43	15.67	15.93	16.18	16.44	16.70	16.96	17.22	17.48	17.74
0.3437	0.2561	14.86	15.11	15.36	15.62	15.87	16.13	16.39	16.66	16.92	17.18
0.3460	0.2511	14.31	14.55	14.81	15.07	15.33	15.59	15.85	16.11	16.37	16.63
0.3482	0.2463	13.77	14.02	14.27	14.53	14.79	15.05	15.32	15.58	15.84	16.10
0.3505	0.2413	13.25	13.50	13.75	14.01	14.27	14.54	14.80	15.06	15.33	15.59
0.3528	0.2364	12.74	12.99	13.25	13.51	13.77	14.03	14.30	14.56	14.83	15.09
0.3550	0.2316	12.25	12.50	12.76	13.02	13.28	13.55	13.81	14.08	14.34	14.61
0.3573	0.2266	11.78	12.03	12.29	12.55	12.81	13.07	13.34	13.61	13.87	14.14
0.3595	0.2219	11.31	11.56	11.82	12.09	12.35	12.62	12.88	13.15	13.42	13.68
0.3618	0.2169	10.86	11.12	11.38	11.64	11.90	12.17	12.44	12.71	12.97	13.24
0.3641	0.2119	10.43	10.68	10.94	11.21	11.47	11.74	12.01	12.27	12.54	12.81
0.3663	0.2071	10.00	10.26	10.52	10.78	11.05	11.32	11.59	11.86	12.13	12.40
0.3686	0.2022	9.59	9.83	10.11	10.38	10.64	10.91	11.18	11.45	11.72	11.99
0.3709	0.1972	9.19	9.43	9.71	9.98	10.25	10.52	10.79	11.06	11.33	11.60
0.3731	0.1924	8.81	9.06	9.33	9.60	9.86	10.13	10.41	10.68	10.95	11.22
0.3754	0.1874	8.43	8.69	8.95	9.22	9.49	9.76	10.03	10.31	10.58	10.85
0.3776	0.1827	8.06	8.32	8.59	8.86	9.13	9.40	9.67	9.95	10.22	10.49
0.3799	0.1777	7.71	7.97	8.24	8.51	8.78	9.05	9.33	9.60	9.87	10.15
0.3822	0.1727	7.37	7.63	7.90	8.17	8.44	8.71	8.99	9.26	9.54	9.81
0.3844	0.1680	7.03	7.30	7.56	7.84	8.11	8.38	8.66	8.93	9.21	9.48
0.3867	0.1630	6.71	6.97	7.24	7.51	7.79	8.06	8.34	8.61	8.89	9.17
0.3889	0.1582	6.39	6.66	6.93	7.20	7.48	7.75	8.03	8.31	8.58	8.86
0.3912	0.1532	6.09	6.35	6.63	6.90	7.17	7.45	7.73	8.01	8.28	8.56
0.3935	0.1483	5.79	6.06	6.33	6.61	6.88	7.16	7.44	7.72	7.99	8.27
0.3957	0.1435	5.50	5.77	6.04	6.32	6.60	6.88	7.15	7.43	7.71	7.99
0.4003	0.1336	4.95	5.22	5.50	5.78	6.06	6.33	6.62	6.90	7.18	7.46
0.4048	0.1238	4.44	4.71	4.99	5.26	5.55	5.83	6.11	6.39	6.67	6.96
0.4093	0.1141	3.95	4.22	4.50	4.78	5.07	5.35	5.63	5.92	6.20	6.49
0.4138	0.1043	3.49	3.77	4.05	4.33	4.62	4.90	5.19	5.47	5.76	6.04
0.4184	0.0944	3.07	3.34	3.62	3.91	4.19	4.48	4.77	5.05	5.34	5.63
0.4229	0.0846	2.66	2.94	3.22	3.51	3.80	4.08	4.37	4.66	4.95	5.24
0.4274	0.0749	2.28	2.56	2.85	3.13	3.42	3.71	4.00	4.29	4.58	4.87
0.4319	0.0652	1.92	2.20	2.49	2.78	3.07	3.36	3.65	3.94	4.23	4.52
0.4364	0.0554	1.58	1.86	2.15	2.44	2.73	3.02	3.31	3.60	3.89	4.19
0.4432	0.0407	1.10	1.39	1.68	1.97	2.26	2.55	2.84	3.13	3.43	3.72
0.4500	0.0260	0.67	0.95	1.24	1.53	1.82	2.12	2.41	2.70	3.00	3.29
0.4568	0.0113	0.27	0.56	0.85	1.14	1.43	1.72	2.01	2.31	2.60	2.90
0.4613	0.0015	0.03	0.32	0.60	0.89	1.19	1.48	1.77	2.06	2.36	2.65
0.4636	-0.0035	-0.09	0.20	0.49	0.78	1.07	1.36	1.65	1.95	2.24	2.53
0.4681	-0.0132	-0.02	0.27	0.56	0.85	1.14	1.43	1.72	2.01	2.31	2.61
0.4726	-0.0229		0.06	0.35	0.64	0.93	1.22	1.51	1.80	2.09	2.39
0.4772	-0.0329		-0.13	0.15	0.44	0.73	1.02	1.31	1.60	1.89	2.19
0.4817	-0.0426				-0.03	0.25	0.54	0.83	1.11	1.40	1.69
0.4862	-0.0524					0.08	0.36	0.65	0.93	1.22	1.50
0.4930	-0.0671					-0.16	0.12	0.40	0.68	0.96	1.25
0.4988	-0.0818						-0.10	0.17	0.45	0.73	1.01
0.5088	-0.1013							-0.09	0.18	0.46	0.73
0.5179	-0.1210								-0.05	0.22	0.48
0.5269	-0.1405									0.01	0.27
0.5360	-0.1602									-0.18	0.08
0.5405	-0.1699										-0.01



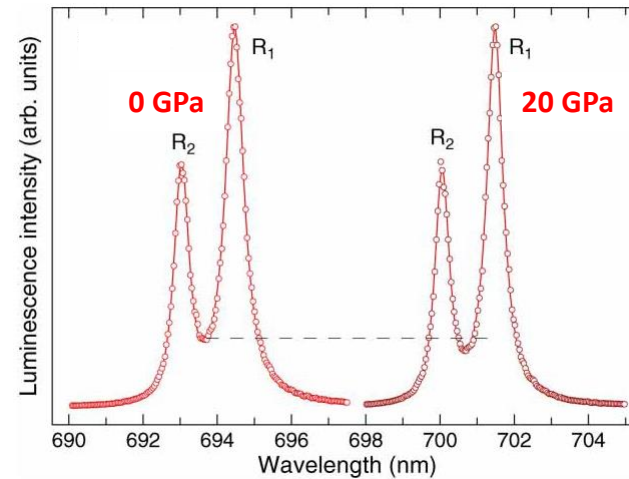
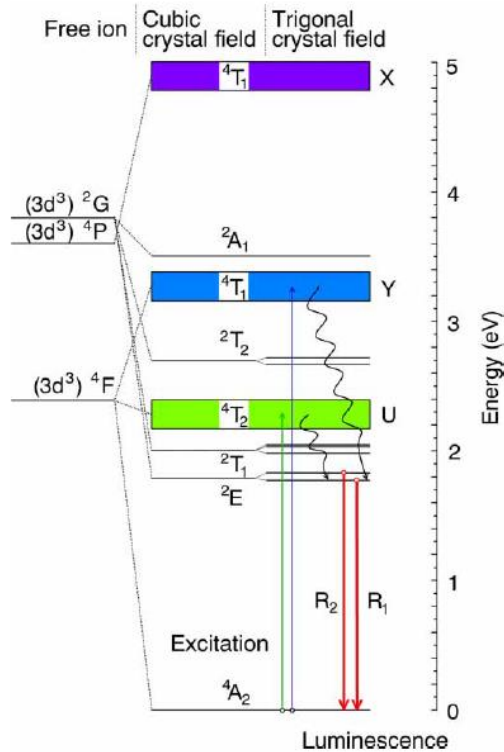
$$P_{\text{Brown}} - P_{\text{Decker}} / P \approx 3\%$$

Probably more accurate than Decker!

The ruby fluorescence gauge

Ruby: $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (« corundum »)

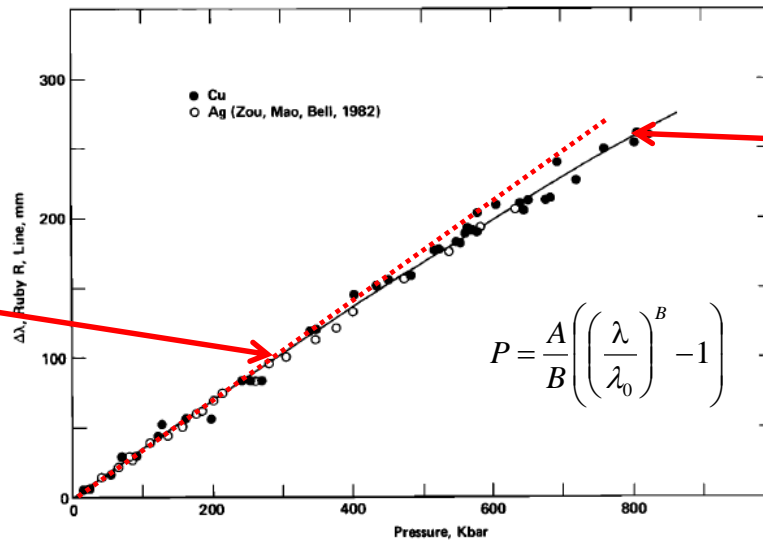
Cr^{3+} : $\sim 0.1\text{-}1\%$



$$\Delta\lambda/\Delta P = +0.365 \text{ nm/GPa}$$

The ruby 1986 calibration (« Mao quasi-hydrostatic scale »)

Mao, Xu, Bell, JGR 91, 4673 (1986)



Initial slope forced to be coherent with Decker scale

Curvature coherent with shock EOS data for V, Cu, Ag

- « The Decker scale is the mother of the ruby scale »

$$P = \frac{A}{B} \left(\left(\frac{\lambda}{\lambda_0} \right)^B - 1 \right)$$

A = 1904 GPa
 B = 7.665

Other fluorescence gauges

Material	λ (nm)	$\frac{d\lambda}{dp}$ (nm/GPa)	$\frac{d\lambda}{dT}$ (nm/10 ³ K)
Cr ³⁺ :Al ₂ O ₃	694.2	+0.365	+6.8



Ruby:
Moderate $d\lambda/dp$
Large $d\lambda/dT$

!

Pressure transmitting media & hydrostatic conditions

Why is this important?

- « Pressure » in physics means almost exclusively hydrostatic pressure: $\sigma = -\delta_{ij} p$

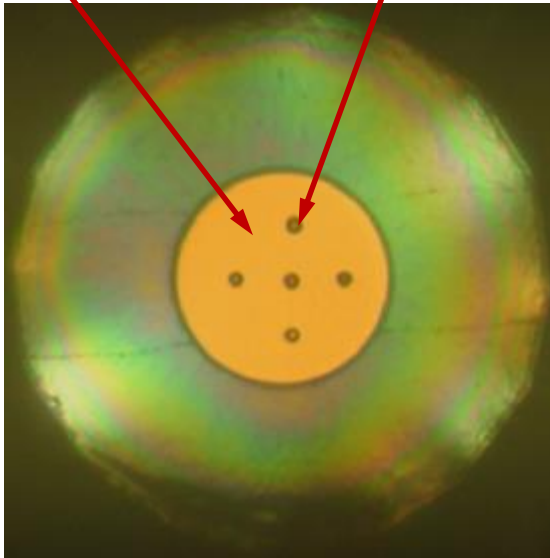
ex: $p = -(\partial E / \partial V)_T$ $B = -(\partial p / \partial \ln V)_T$

- Hydrostatic P is reproducible and easy to characterize other P-conditions not/only with great difficulties

Characterizing hydrostaticity

Example 4:1 methanol–ethanol (Piermarini 1973)

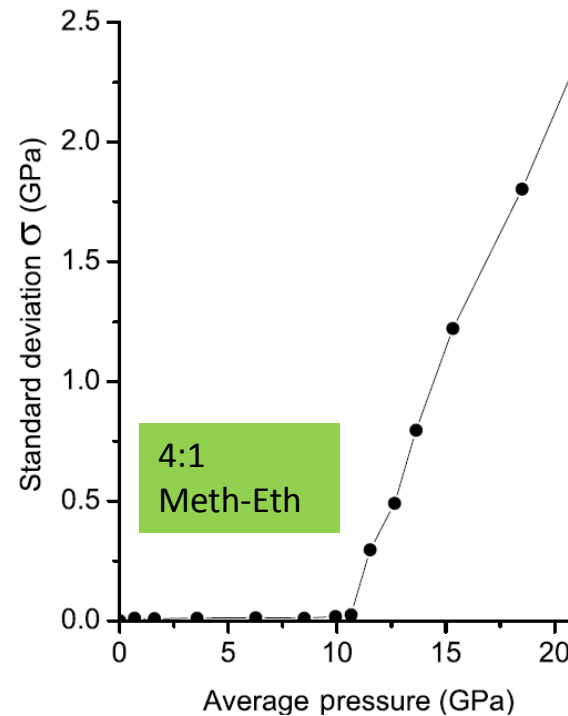
fluid N ruby balls



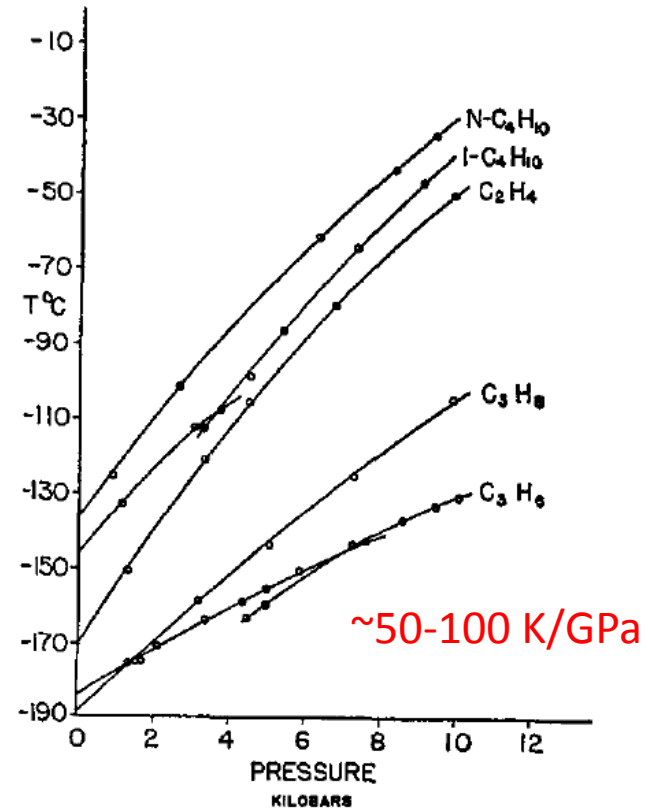
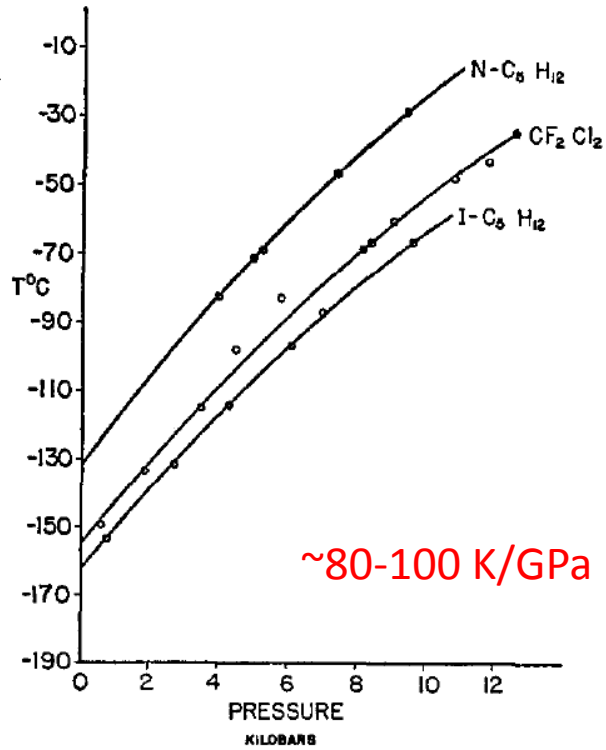
© K. Takemura

S.K., J.C. Chervin, P. Munsch, G. Le Marchand,
J. Phys. D: Appl. Phys. 42, 07413 (2009)

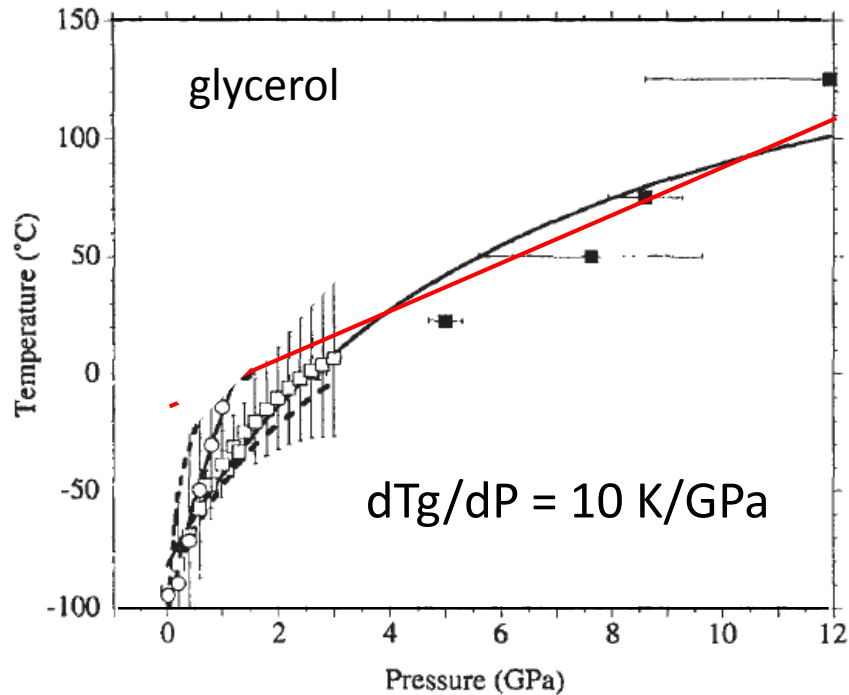
$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (P_i - \bar{P})^2}$$



Melting curves: pure substances



Glass forming liquids: P-dependence of T_g



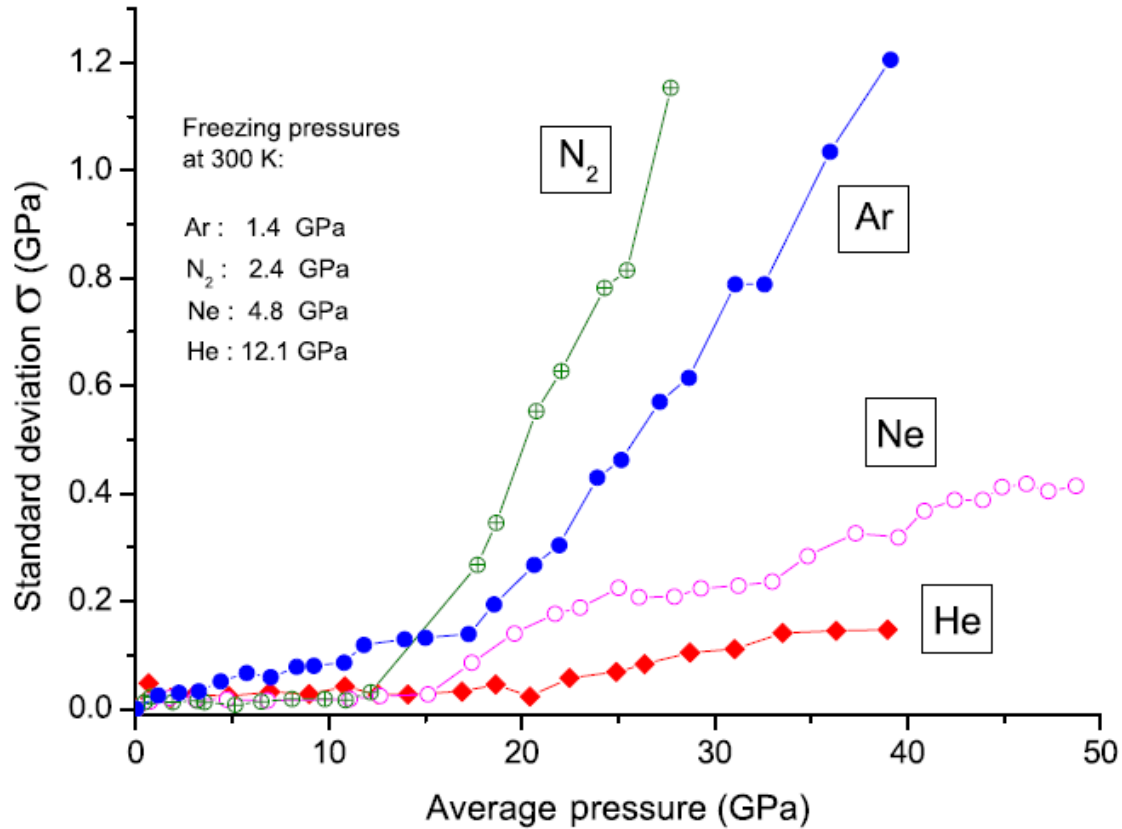
Cook et al. , JCP 1994

4:1 Meth-Eth: $\approx 11 \text{ K/GPa}$

DAPHNE: $\approx 25 \text{ K/GPa}$

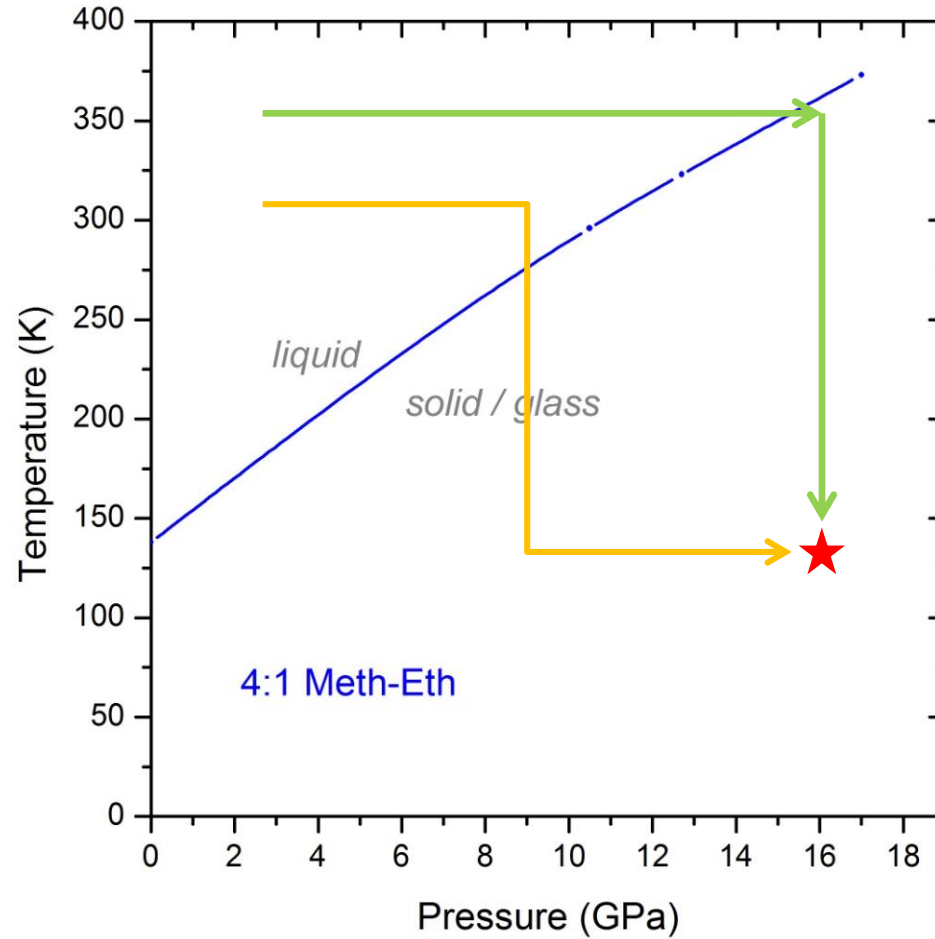
Much smaller than melting lines!

Compressed gases as PTM



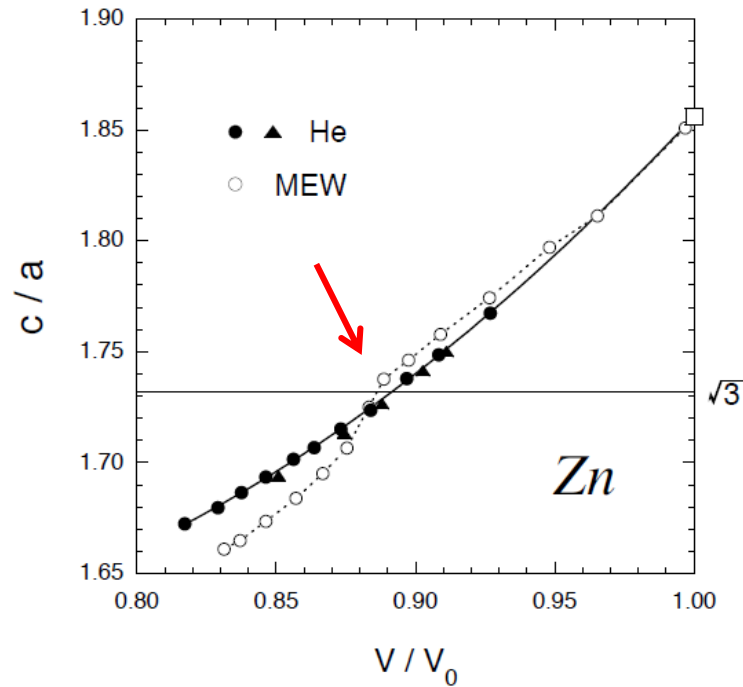
S.K., J.C. Chervin, P. Munsch, G. Le Marchand,
J. Phys. D: Appl. Phys. 42, 07413 (2009)

ME: Optimizing compression procedure

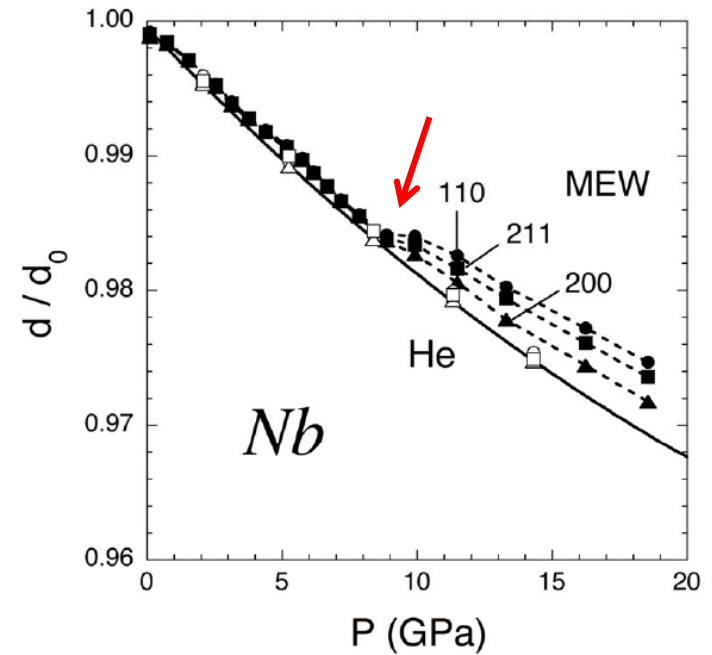


4:1 Methanol-Ethanol, see: S.K. et al., High Press. Res. 29, 649 (2009)

Pitfalls I: Freezing of the PTM



K. Takemura, PRL 1995
K. Takemura, Proc. AIRAPT Conf. 2005



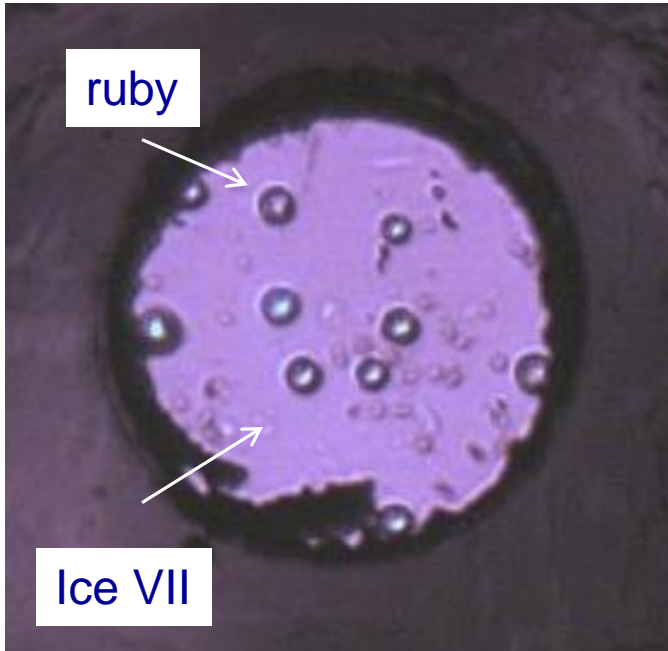
K. Takemura, JPSJ, 2007

Pitfalls II: No PTM

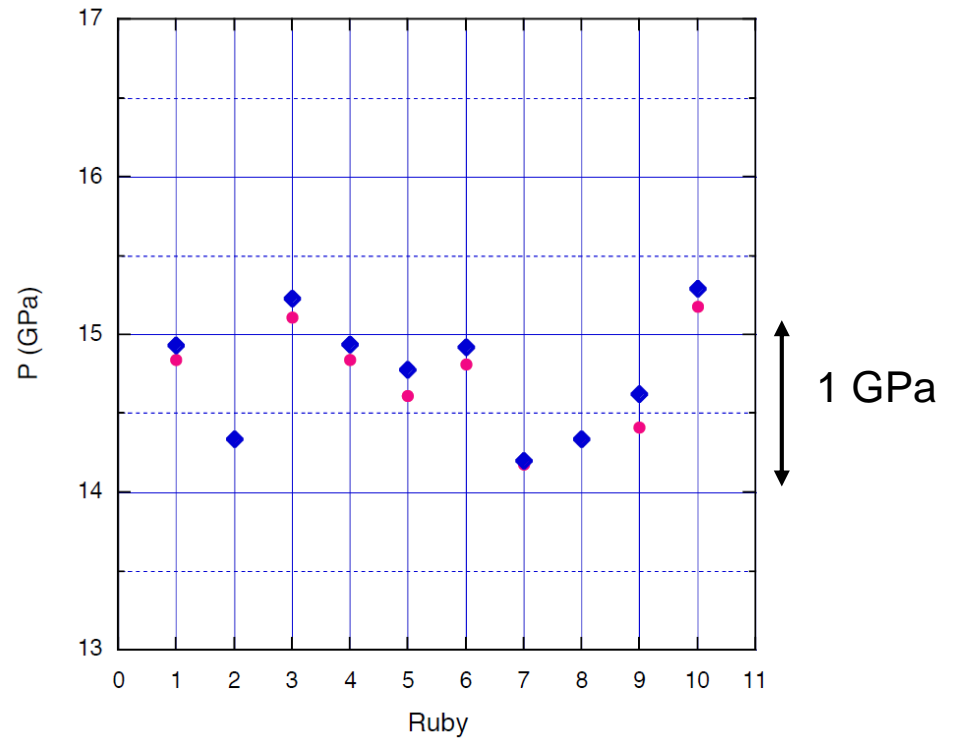
Example: EOS of ice VII

Reference	Method and EoS	V_0 (Å ³)	B_0 (GPa)	B_0'	P range (GPa)
Olinger & Halleck (1975)	D, emp ¹	42.6 (10)	12.5 (3)	5.6 (1)	2.6–8.15
Munro <i>et al.</i> (1982)	D, emp ²	42.7	15.78	4.11	2.3–36
Liu (1982)	D, BM3	42.1 (2)	24.0 (9)	4.50	2.15–50.4
Hemley <i>et al.</i> (1987)	D, BM3	40.9 (10)	23.7 (9)	4.15 (7)	4.3–128
Fei <i>et al.</i> (1993)	D, BM3	40.9 (7)	23.9 (7)	4.2 (5)	3.16–18.55
Shimizu <i>et al.</i> (1995)	B		13.7 (4)	5.33 (9)	2–7
Loubeyre <i>et al.</i> (1999)	D, V	48.2	4.26	7.75	2.2–170
Pruzan <i>et al.</i> (2003)	D, V	42.1 (7)	14 (2)	5.6 (2)	2–120?
Frank <i>et al.</i> (2004)	D, BM3	41.2 (3)	21 (1)	4.4 (1)	6.57–60.52
Fortes <i>et al.</i> (2012)	D, M	42.5 (3)	13 (1)	5.5 (3)	1.97–6.94
Bezacier <i>et al.</i> (2015)	D, B	41.3 (1)	20.8 (3)	4.0	2.1–10.1

(adapted from Fortes 2012)



Takemura & Klotz, unpublished



Pitfalls III: Penetration

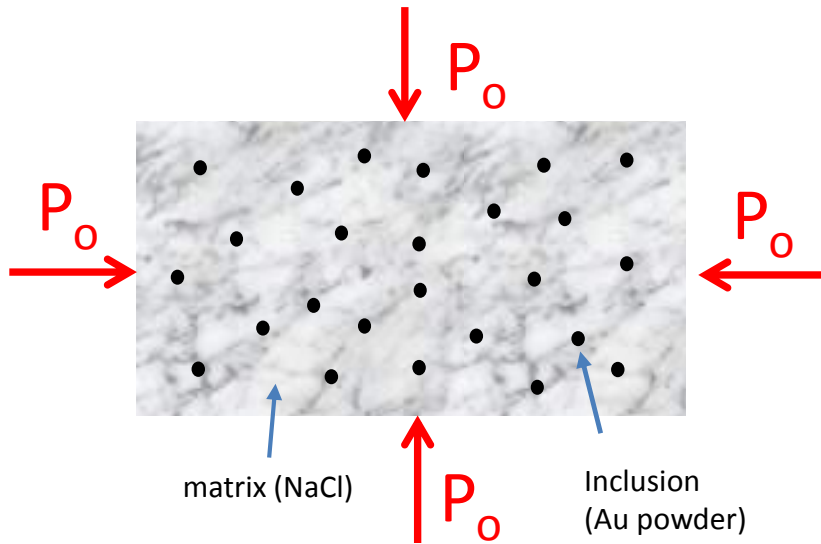
Many many other examples: ex: zeolites, glasses

Message: check crystal structure first!

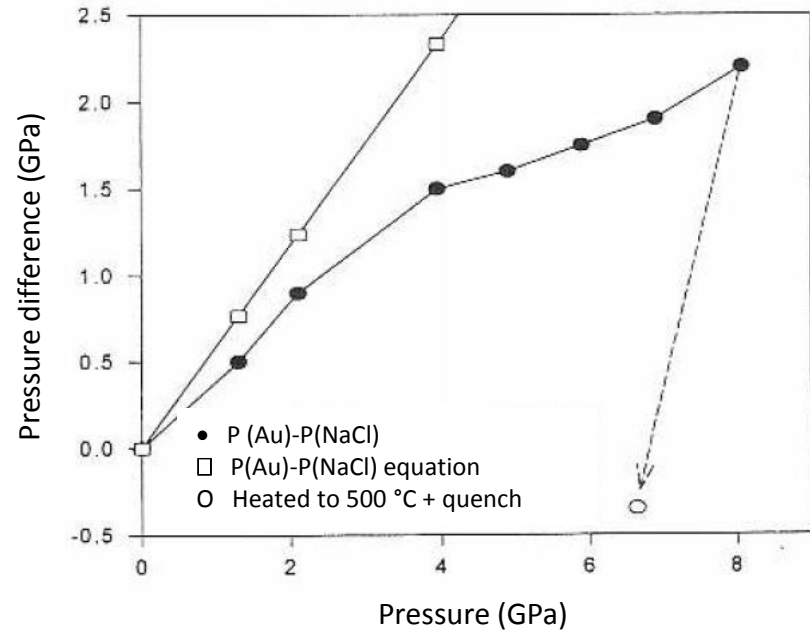
Pitfalls IV: The Lamé effect

→ solid PTMs

Ex: Au powder in NaCl



Wang & Weidner, Geophy. Monogr., 1998



$$P_i = P_o \left(1 + \frac{4\mu_m}{3B_m} \right) / \left(1 + \frac{4\mu_m}{3B_i} \right)$$

Thank you !
Questions ?