

High pressures and the structure of solids of geochemical and geophysical interest

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Abstract

Pressures of 10 GPa and above can bring about phase transformations in many oxides, an effect of great interest to geochemists and geophysicists. We can interpret such behaviour as due to the differential compressibility of 'anion' and 'cation' leading to a progressive rise in radius ratio with pressure, and hence, on the classic crystallochemical picture, eventually to an increase in co-ordination number (though with complications which make prediction difficult). More generally, pressure affects Gibbs free energy G directly; for oxides a pressure of 5 GPa gives, very roughly, the same contribution to G as 100 °C in temperature (though with opposite sign). Thus high pressure significantly affects the shape and structure of phase diagrams, showing increasingly important effects above, say, 10 GPa—but again prediction can be difficult. However these two complementary approaches to the effects of pressure, helpful though they can be conceptually, are 'crystal-based' and totally neglect another rather little-known but potentially important effect—the formation of amorphous solids; 'polymers' and glasses. Since amorphous materials are 'non-equilibrium' they are not readily dealt with theoretically; also, since they are difficult to detect by standard crystallographic techniques, they can be overlooked experimentally. The pressure-induced formation of amorphous solids could have significant implications for both geochemistry and geophysics.

KEYWORDS: high pressures, Gibbs Free Energy, solids, polymers, glasses.

THIS paper discusses in a general way how one can understand some of the changes in structure brought about by pressure. The simplest approach is in terms of classical chemical crystallography, with pressure leading to a progressive increase in radius ratio and, hence, change of coordination. However there are several complicating factors here which are usually totally neglected. At a more fundamental level one can consider changes in free energy induced by pressure. As we shall see this approach requires one to consider the phase diagrams of the system as a whole rather than that of one specific phase in it—but these diagrams have been relatively little-investigated at high pressures. Finally, amorphisation brought about by pressure poses some fascinating problems, but again proves to be a much more complex set of phenomena than is usually realised.

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The chemical crystallographic approach

This deals essentially with close-packed structures; these of course are what tend to form at high pressures. The basic assumptions here might appear improbable but have a long and respectable history.

1. Solids are treated as ionic, the ions being spherical and incompressible in the first instance.
2. Ions of opposite charge maintain contact with each other. This leads to the critical radius ratio: if this is exceeded the co-ordination number is forced to increase. Therefore, if a table of ionic radii was used, it should be possible to plot a group of compounds with similar formulae in terms of $r_{\text{anion}}/r_{\text{cation}}$, and expect the structures to divide into fields separated by lines of slope 0.414, etc, showing 4-, 6- and 8-co-ordination (Fig. 1). Fig. 2. shows a plot for a large number of AX_2 compounds, which includes that important material, SiO_2 . The radii used are essentially those

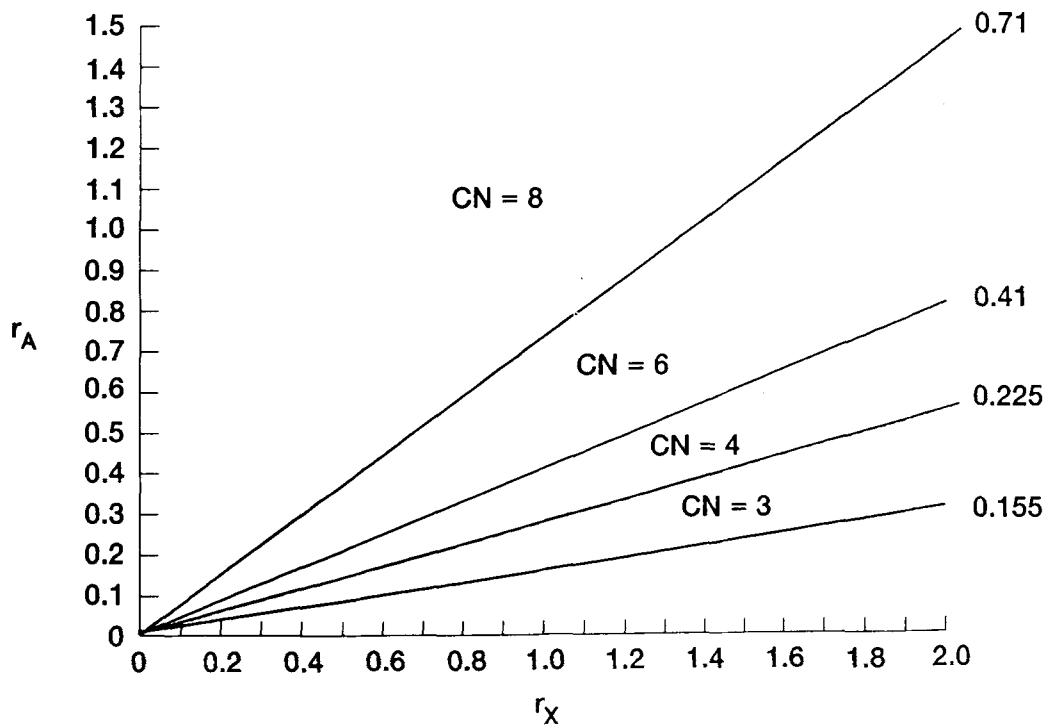
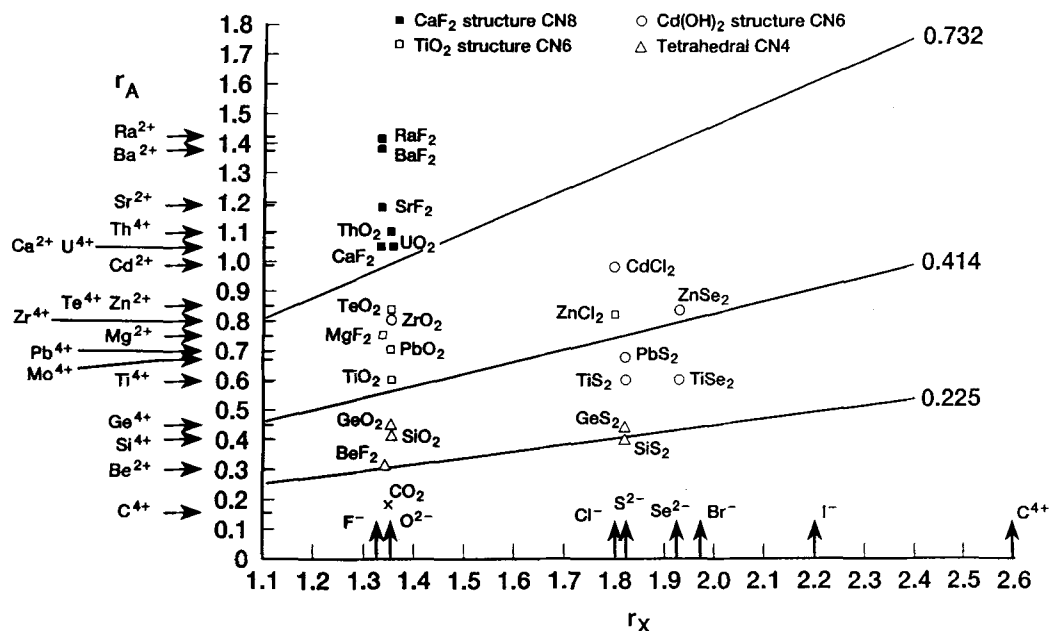


FIG. 1. Idealised plot for anion vs. cation radii.

FIG. 2. Plots for AX_2 compounds.

due to Wyckoff (1965) plus a few from Ahrens (1952) and will be discussed in more detail later. Other tables of radii could of course be used, e.g. Shannon and Prewitt (1969).

Fig. 2 shows general behaviour very much like that predicted by Fig. 1; it falls into fields with 4-, 6- and 8-fold co-ordination, except that the materials often show higher co-ordination than expected. Qualitatively this is easy to understand in that the large, expanded, negatively charged anions will be far more readily deformable than the contracted positively charged cations, so that the forces holding the solid together will result in the anions behaving as if they were consistently smaller.

What might Fig. 2, which of course is a 'one-atmosphere' plot, suggest regarding the effect(s) of pressure? Interatomic distances are reduced by pressure and the argument about the greater deformability of negatively charged anions would suggest that this should be associated with an increase in effective radius ratio, i.e. pressure should shift a given compound to the left in Fig. 2, and therefore, eventually, into a region of higher co-ordination number. Such behaviour is of course observed experimentally in a number of cases, perhaps the best known example being the pressure-induced transformation of tetrahedral Si in SiO_2 , e.g. in quartz, to octahedral Si in

stishovite, but even this example is complicated by the intermediate formation sequence quartz-coesite-stishovite. The simple crystallographic approach would not readily predict the formation of coesite. It should be pointed out that at some very high pressure CO_2 will adopt a tetrahedral coordination.

The radii used in Fig. 2 are given in Fig. 3 which is a plot of Wyckoff radii (plus some from Ahrens) for all the elements. Some comment on these radii is essential. Firstly, although it is assumed to be a plot of ionic radii, Wyckoff radii are in fact a self-consistent set of radii, carefully derived and adjusted from experimental values of lattice parameters for a variety of compounds. How 'good' they are in reproducing 'reality' can be seen from Fig. 4 which shows the excellent agreement between sums of Wyckoff radii and observed interatomic distances for more than 50 compounds with the rock salt structure. What requires special note here are the distinctly marked points which refer to the PbS group of compounds, which, though very definitely not ionic by any normal definition of that term, fall very well on the correct line in Fig. 4.

This brings us to the matter of deviation from purely ionic bonding. Here some useful guidance can be obtained from a non-standard treatment of 'electronegativity difference'. Though normally

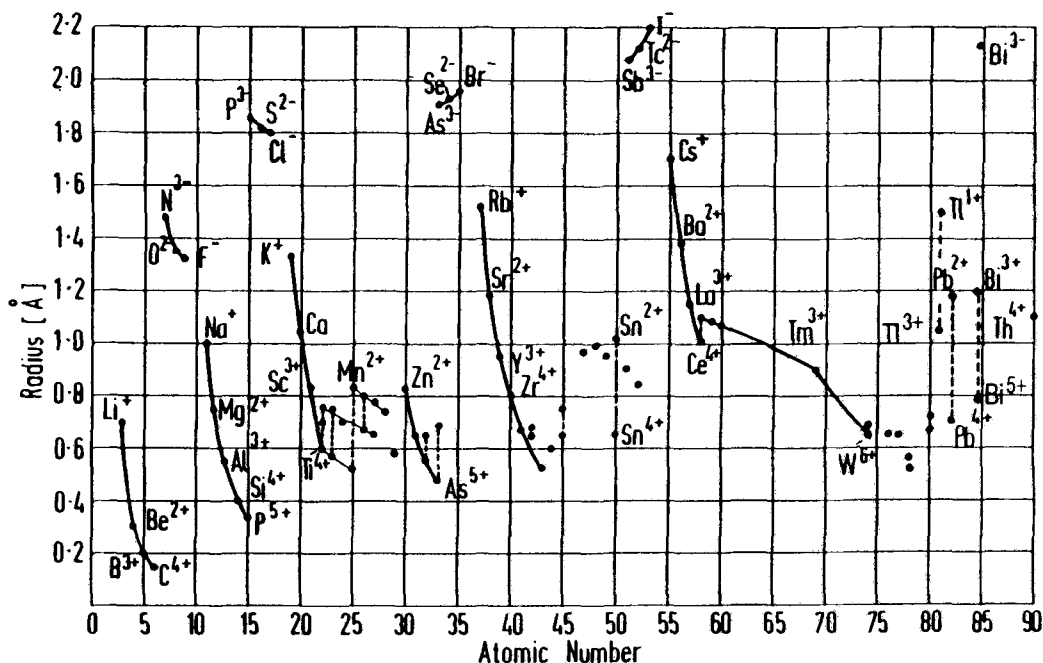


FIG. 3. Wyckoff crystal radii.

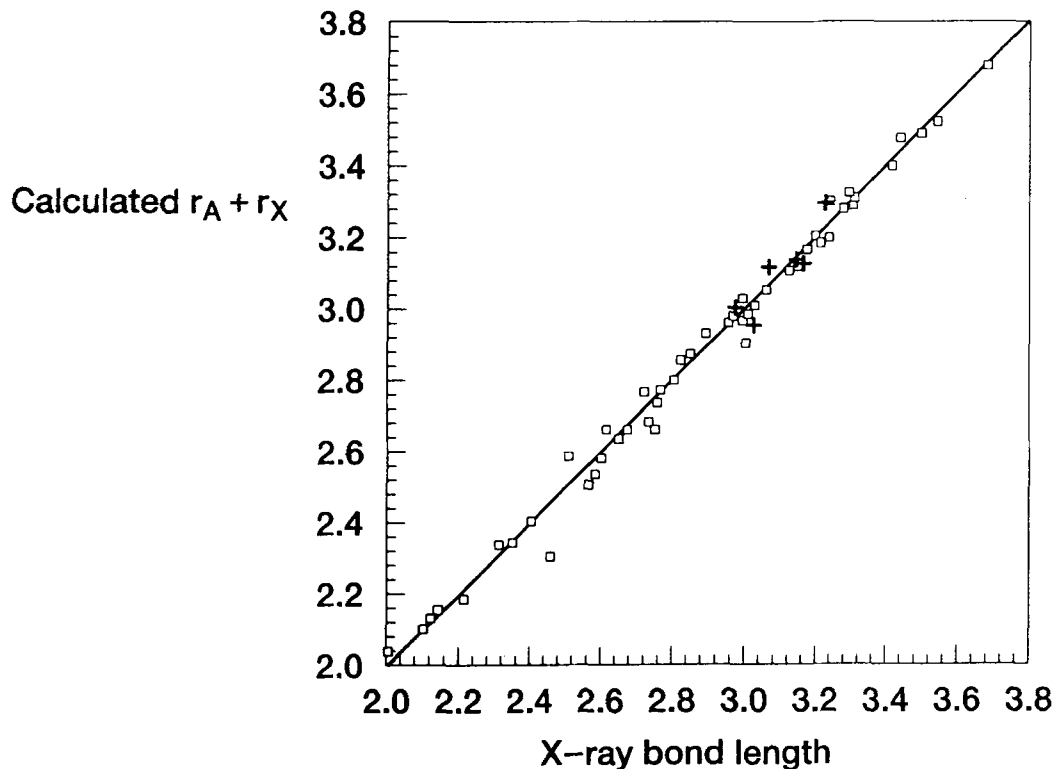


FIG. 4. Calculated vs. experimental bond lengths for crystals with NaCl structure (Wyckoff crystal radii).

neglected, the effects associated with this concept have a significant influence on effective radii. Conceptually, electronegativity is best looked on as an inverse measure of effective screening of nuclear charge by valence electrons, as pointed out by Hartree in the 1930s. On his argument, in elements having large numbers of *s* and *p* valence electrons, e.g. oxygen, chlorine, these electrons (on account of correlation effects) do not screen each other with unit efficiency from the (balancing) nuclear charge and therefore experience a much larger effective charge than elements with few electrons, e.g. Mg.

Consider, for example, the formation of the compound MgO in which Mg with two valence electrons screens its core so much more effectively than O with six, that in the compound almost all the electron density associated with the Mg atoms becomes transferred to the oxygen *p*-orbitals, giving essentially ionic bonding. What should be noted here is that this can be described in terms of the setting up of an equilibrium: the reduction of electron density in the Mg *p*-orbitals causing a rise in effective core screening until it

becomes equal to that of oxygen, which has fallen as electron density has transferred to its orbitals.

This concept of 'equalisation of electronegativities' when a compound forms is particularly important in our context.

Without examining its derivation, Fig. 5 plots the electronegativities of the elements. Let us use this to discuss for example the solid solution series $(\text{Fe}^{\text{II}}, \text{Mg})\text{SiO}_3$. From Fig. 5, Fe^{II} has a significantly higher value of electronegativity than Mg (1.7 versus 1.2) so that $\text{Fe}^{\text{II}}\text{-O}$ bonding can no longer be considered purely ionic. 'Equalisation of electronegativities', then, means that as Fe^{II} content increases the negative charge on the oxygen in the lattice must decrease, which will lead to a decrease in its effective radius, i.e. an increase in effective radius ratio. It is this effect, rather than the slight increase in radius of divalent Fe compared with Mg (0.80 versus 0.75), that is responsible for the lower pressures required to stabilise $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ spinel than is the case with pure Mg_2SiO_4 , although both effects must be taken into account.

This correction becomes increasingly import-

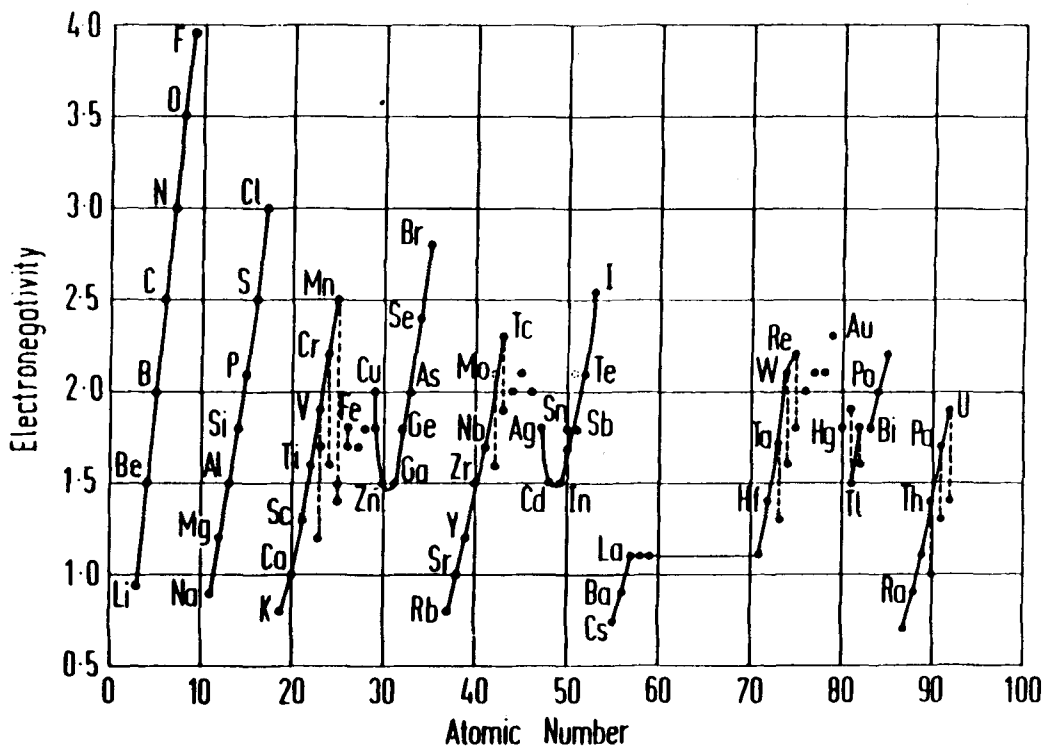


FIG. 5. Electronegativities of the element.

ant as electronegativity differences fall below 2.0 units, which is often taken as a guide to the limit below which at least some covalency needs to be taken into account in bonding, i.e. the material is no longer effectively ionic. What these arguments emphasise is that the substitution of elements into complex minerals is accompanied by changes in the effective charge (and hence size) of the elements of the host lattice.

What is being suggested is that radii alone are not a good guide to co-ordination number (particularly in ternary and more complex compounds) because although, as indicated earlier, they are reasonably self-consistent, they represent compromise values which may require significant correction for electronegativity effects. Another area where this holds true also, is for elements showing variable valency. For these there is a general rule, readily verifiable from Fig. 5, that the higher the valence, the higher the electronegativity—exactly what would be expected on the Hartree picture (electrons in orbitals localised on atoms and not taking part in bonding will screen nuclear charge more effectively, i.e. give a lower electronegativity value than those that do take part). Manganese is a

particularly extreme case here. When divalent it has a low electronegativity value of 1.4, similar to that for Zn, 1.5, which it resembles chemically. With a valency of 7, however, it is a pseudo-halogen and with the high electronegativity of 2.5 approaches the values of iodine and bromine which it resembles in chemical behaviour.

On the basis of such arguments, one would expect, therefore that radii for variable valence atoms, which from Fig. 3 fall with increasing valence (compare divalent and heptavalent Mn which show a relatively large radius for Mn^{II} , 0.83, and a small one for Mn^{VII} , 0.46) and which have been obtained self-consistently from bond lengths in a variety of compounds, may require significant correction for the electronegativity factor when used in solid solution formation.

Clearly this kind of approach is essential in any discussion of the pressure stabilisation of, say, (Mg, Fe) spinel solid solutions, as one possibility, where the oxidation of divalent Fe^{II} could lead to the presence of 3-valent Fe and vacancies, as in 'FeO' under one atmosphere conditions, which could significantly affect matters. The argument here is that the increase in electronegativity associated with increase in Fe valence from 2 to 3

will raise the average oxygen negative charge because of the principle of equalisation of electronegativities discussed earlier. That charge determines its effective radius which also will increase, so that such oxidation should increase the pressure required to stabilise the spinel structure. This conclusion is rather different to what might be expected on the basis of radii only but provides a better guide, at least for cases with some well defined excess or deficit of pressure. What will occur in practice however, close to the transition boundary will depend on a delicate balance of energies including that required for the formation of vacancies and shear forces at grain boundaries both grown in, and due to volume changes at the transition.

Free energy considerations

In general terms what happens to free energy under the application of pressure is reasonably straightforward. The Gibbs free energy equation:

$$G = U + PV - TS \quad (1)$$

is certainly well known, but except by geoscientists, that equation is rarely thought of as implying a situation in which the pressure term makes a contribution comparable with, or even greater than, the temperature-entropy term. However, even with oxides which tend to be incompressible, this situation can hold, particularly for pressures above 20 GPa. In this range we should not think of 'thermodynamics' but 'thermobarodynamics' in order to emphasise that pressure plays a significant role. As a rough indication of the magnitudes involved, for many oxides the application of a pressure of 10 GPa alters free energy by a similar amount to the change brought about by raising temperature by 100 to 200 °C—note of course the opposite formal sign in equation (1). In a few special cases however, where the material contracts on melting, like the element silicon below about 1 GPa, melting point is reduced by the application of pressure, e.g. at 1 atm silicon melts at 1420 °C but by 5.5 GPa the melting point has fallen to 1080 °C. Something else that can be overlooked is that SiO₂ can be reduced at very low oxygen partial pressures, and if such conditions can be encountered in the upper mantle the presence of a liquid phase could prove important and unexpected. I shall return to this point subsequently.

Silica provides a highly interesting example of a relatively simple AX₂ compound which shows a large number of polymorphs induced by the application of pressure: these, including coesite and stishovite, as well as the recently discovered

form with CaCl₂ structure, are only stable above ~10 GPa (Suchida and Yagi, 1989). Presumably at some higher pressure, one would expect from Fig. 2 that a fluorite-like or pyrite-like form would be obtained. One can rationalise this situation in terms of a 1-atmosphere free energy plot of the type shown in Fig. 6. As pressure is increased the terms in the Gibbs Free Energy equation (1) progressively favour the next phase 'upwards'. (This is at constant temperature, e.g. 300 K; at higher temperature some inversion of the order might be possible, but there is little information available.)

In Fig. 6, reference is made to the whole system rather than SiO₂ alone in order to emphasise that only two compositions, Si and SiO₂ are usually considered. However, the existence in analogous heavier cation phase diagrams, e.g. Sn-SnO₂ or Ge-GeS₂, of an intermediate 1:1 compound (SnO, GeS), suggests that at higher pressures, when the radius ratio would be adequately increased, a new phase SiO could become stabilised.

These, of course, are crystallochemical arguments, but simple free-energy considerations indicate how such a new phase would manifest itself as pressure is increased. Returning to Fig. 6, a dotted free energy curve centred on the 1:1 position is sketched for the 300 K 1-atmosphere situation in which solid SiO is never stable. Raising the temperature drops the curve for the liquid sharply with respect to the curves for Si and SiO₂.

One interesting peculiarity of the system however is that the freezing point of silicon is reduced by the pressure as noted previously, i.e. pressure results in a further anomalous lowering of free energy of the liquid on the silicon side of the Fig. 6. This might be thought of as being of little geophysical interest were it not that at high temperatures SiO₂ can be reduced by hydrogen or

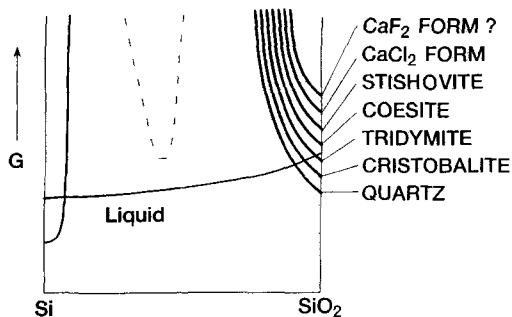


FIG. 6. Free energy variations in the system Si-SiO for 1 at 300K.

carbon to give mixtures of Si liquid and SiO_2 solid. There appears to have been little or no experimental work on such mixtures beyond some preliminary and unpublished experimental runs carried out some time ago, by this author, heating specimens of amorphous 'SiO' (a brown amorphous solid available from suppliers of materials for vacuum deposition) under pressure. These showed that at 5.5 GPa and 500°C there was no change to the 'SiO' but that at 5.5 GPa and 1100°C it separated into Si + SiO_2 , the silicon being liquid under these conditions. This is just what one would expect from Fig. 6 in that as previously noted at 5.5 GPa the melting point of Si has fallen to 1080°C. That, however, is well above the minimum melting point of Si as a function of pressure, which is near 800°C at pressures of about 10 GPa. Such a low-temperature liquid phase, presumably associated with the grain boundaries, could have significant effects on the mechanical properties of silica rich rocks but, clearly, only if strong reducing conditions were encountered. However, perhaps just such conditions are needed for the synthesis of diamonds!

Application of very high pressures will progressively lower the free energy curve of the SiO phase with respect to the liquidus line until at pressures, probably in excess of 20 GPa, it does become a stable solid, but one that would be melting incongruently. This leads to a new phase diagram for Si-SiO₂ of the type shown in Fig. 7a, with SiO being formed peritectically. At still higher pressures this would be expected to change to Fig. 7b, SiO becoming a congruently melting phase.

It is interesting to note that SnO and GeS, which can be thought of as existence theorems for SiO, are both layer lattices with unusual semiconducting and mechanical properties (crystalline SnO rubbed between the fingers feels like butter, and is a better solid lubricant in that sense than the much publicised MoS₂, it cannot however be

used as a lubricant as it readily reoxidises in air to SnO₂, which is a good abrasive). I would therefore argue that the formation of crystalline SiO within the grain boundaries of silica-rich rocks could be of significant importance to their mechanical properties—but again, this requires rather strong reducing conditions and at pressures far higher than those discussed previously for the presence of low melting silicon liquid.

Similar arguments of course can be applied to other more complex systems. Polymorphism, i.e. change in structure as from ilmenite to perovskite, in, say, $(\text{Fe,Mg})\text{SiO}_3$, would be expected on free energy or crystallographic arguments. Unfortunately, accurate data on the basic properties of the high pressure phases are rarely available and to the knowledge of this author no proper free energy calculations have been made which could be used predictively in anything beyond a qualitative sense. Some attention needs to be paid to the possibility of the pressure induced formation of new phases. Here, as pointed out in connection with the example previously discussed, of the possibility of formation of a SiO layer lattice phase in the Si-SiO₂ system, the best clue as to possibilities can be obtained from consideration of 'heavier cation analogue' 1-atmosphere phase diagrams. In the case of silicates, this puts some emphasis on germanate systems but if an insight is to be achieved, into the experimental implications of the 100 GPa pressure region that is beginning to open up, there is a need to look to still heavier analogue systems: stannates or zirconates perhaps. For example, Fig. 8 shows the 1-atmosphere MgO-SiO₂ system. For comparison that CaO-TiO₂ system (Fig. 9) shows a much more well-expressed 1:1 phase CaTiO₃ with a maximum melting point which has perovskite structure, the disappearance of a 2:1 phase-like forsterite, and the beginning of stability for 2:3 and 4:3 phases formed peritectically. Moving still deeper in the Periodic Table to the SrO-ZrO₂

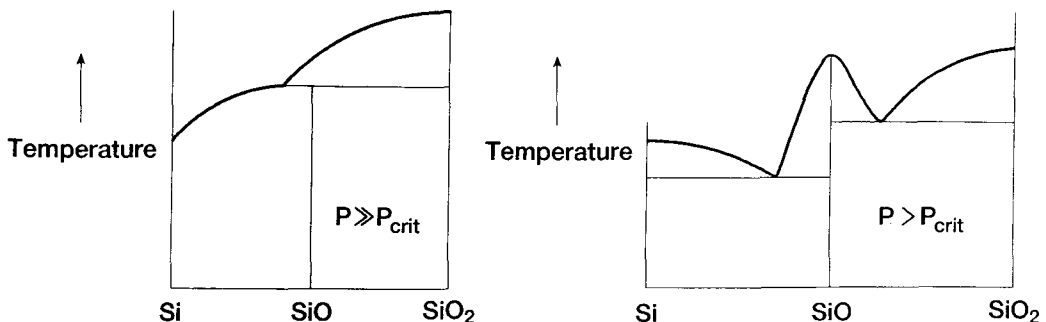
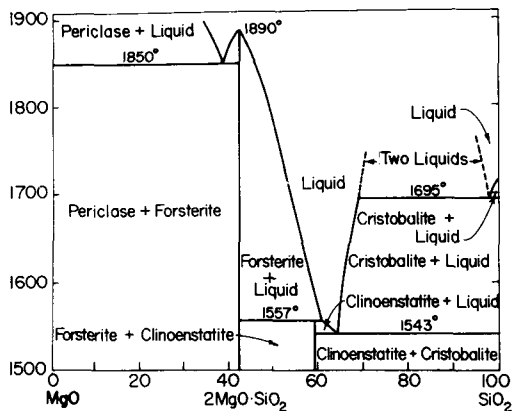
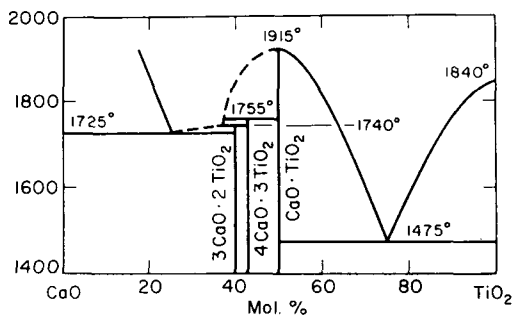
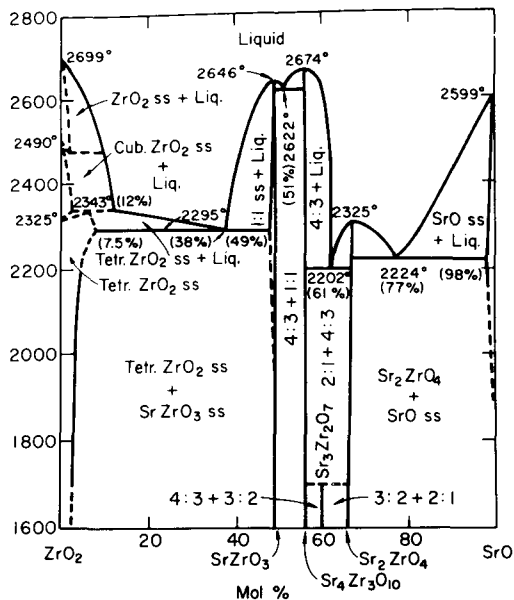


FIG. 7(a). Effect of pressure on stability of new (b) intermediate compound.

Fig. 8. MgO-SiO₂.Fig. 9. CaO-TiO₂.

system, Fig. 10, we find a very stable 1:1 SrZrO₃ with perovskite structure, an even more stable 4:3 phase, Sr₄Zr₃O₁₀, and a reasonably stable 2:1 phase Sr₂ZrO₄. These analogue systems can be considered, in a sense, as confirming the stability of MgSiO₃ in a perovskite structure to extremely high pressures, but suggest in the MgO-SiO₂ system at very high pressures, phases with a variety of possible stoichiometries could make their appearance but always to the MgO-rich side of MgSiO₃. Only if we were to be concerned with the MgSiO₃-SiO₂ side of the system could we conclude that new phases are not likely to be encountered.

Finally, an obvious but frequently overlooked effect of high pressures is that they tend to raise melting points. (Silicon, like water, is exceptional in the overall context.) However this does not prevent the formation of deep-lying eutectics, and this author believes that the investigation of such eutectics warrants more attention than it has so far received. Fig. 11 shows the Al/Si system at 0 and 5.5 GPa (Lees and Williamson, 1984). The

Fig. 10. SrO-ZrO₂.

problem here is that theory provides little guidance: the theoretical treatment of liquids is far less advanced than that of solids, and a eutectic corresponds to a particular stabilisation of the liquid state. While it is obviously of interest to geoscience to be aware of the occurrence of deep-lying eutectics which could 'lubricate' grain boundaries, aiding plastic deformation, there is a further implication (discussed in the final section) that they could also be associated with glass formation.

Pressure-induced amorphisation

I should like to distinguish between three different groups of amorphous solids produced by the action of pressure polymers, shock-quenched glasses and 'true' glasses. All of these materials could be important because:

- they are difficult to detect by standard crystallographic and mineralogical techniques, and hence could be overlooked;
- very little is known about their (P, T) range (or even of their existence) and their modes of crystallisation;
- their mechanical properties will necessarily be different from those of crystalline solids, particularly in the case of the true glasses, and this could

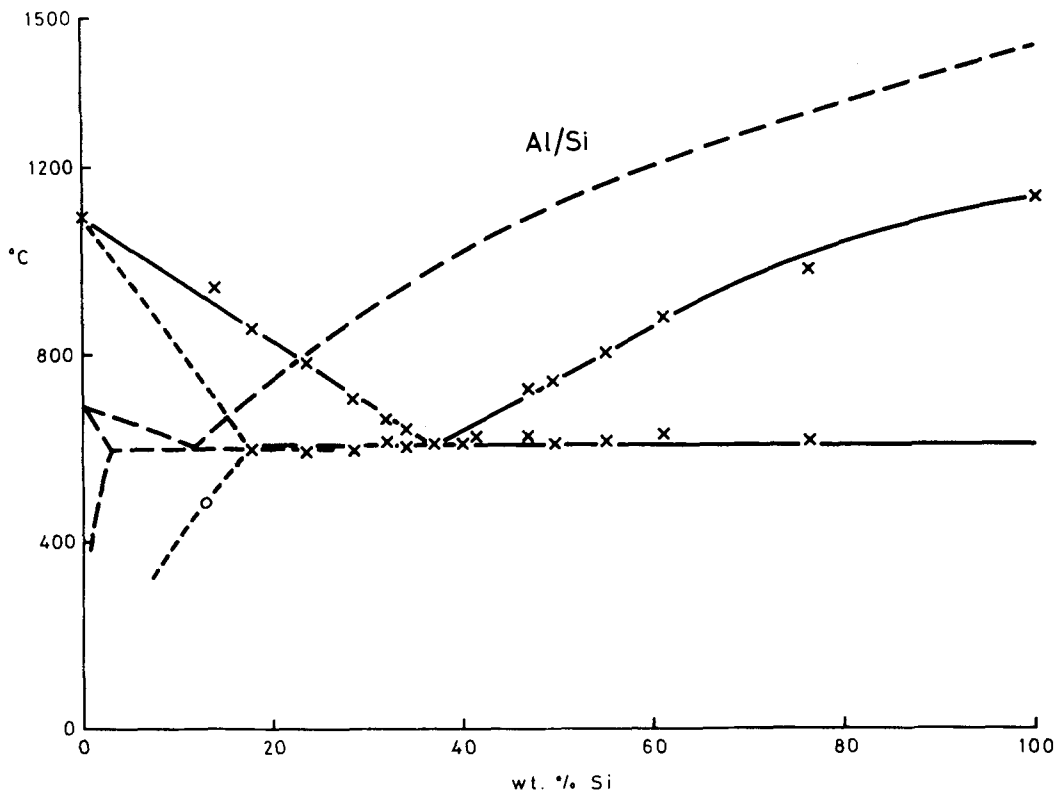


FIG. 11. Al/Si phase diagram at 1 atm (dashed) and 5.5 GPa (solid).

prove of significant importance for geophysics in terms of plastic deformation of rocks.

Pressure-induced polymers

The first pressure-induced polymer was carbon disulphide, which was discovered many years ago (Bridgman, 1941), but remains surprisingly little-investigated. It is formed by pressurising this simple organic compound to above 3 GPa at room temperature: it is recoverable at 1 atmosphere, an inert black solid with poor electrical conductivity. Its (P, T) range of stability is unknown; presumably it decomposes in some way at high temperatures, and at high enough pressures and temperatures may give crystalline forms of carbon sulphur compounds—there could be interest in pursuing such lines of investigation, but the unpleasant toxicity of CS_2 needs to be borne in mind.

Of far more relevance, probably, is the polymer of carbon monoxide, discovered recently by Katz *et al.* (1984) and Mills *et al.* (1984). CO gas, compressed above ~ 5 GPa at low temperatures gives a fascinating yellow amorphous solid. This also can be recovered at 1 atmosphere, when

it appears to react slowly with atmospheric moisture and to decompose thermally or photochemically in visible light, turning orange, purple and black in the process. Initially it was thought to be a sub-oxide of carbon such as C_3O_2 but subsequent work showed 1:1 stoichiometry. The (P, T) stability range of this polymer remains unknown, but presumably there must be some reasonably extended range in P and T over which it will form. This deserves further investigation because if it could be established that this range could extend to high temperatures, e.g. 1000 °C at, say, 10 to 20 GPa, since the presence of such polymer might affect the interaction between silica and carbon (e.g. diamond) under neutral or reducing conditions. Under 1 atmosphere conditions, silica and carbon react strongly at and above 1000 °C to produce gaseous SiO and CO. The SiO of course gives a well-known amorphous solid discussed earlier, but if CO under pressure gives a solid polymer rather than a gas, a totally amorphous solid mixture could result. Such a mixture could conceivably have a lower free energy than a mixture of SiO₂ and C, but this remains a wild speculation in the absence of

experimental information, and of my own finding, described earlier, of the instability of amorphous SiO above the silicon liquidus line.

'Shock-quenched' amorphous solids

These fall into a very different category, in a sense constituting a new class of amorphous solids since they are of very recent discovery; however there can be little doubt that in behaviour they can be readily linked into what is known of a range of other amorphous solids. They are all produced at low temperature, i.e. room temperature or below, and from optical studies of the transformation in diamond anvil cells appear to be formed, in most cases, by what in effect is temperature quenching of the presumably 'superpressed' low pressure, low co-ordination number form to a higher co-ordination number. It appears very unlikely that such materials are glasses, though there has been a strong tendency to call them that—glasses have quite specific properties, as will be discussed later. These materials are almost certainly typical temperature-quenched amorphous solids. This means that on heating to a temperature at which significant atomic diffusion can occur (e.g. near half the melting temperature in K) they will recrystallise, showing a T crystallisation and not a glass transformation temperature, T_g . This point of course requires experimental investigation.

Thus the quartz form of silica undergoes progressive and eventually total and permanent amorphisation at pressures around 15 GPa (Hazen *et al.*, 1989), while crystalline anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) requires rather higher static pressures (Williams and Jeanloz, 1989): 22 to 28 GPa. A member of a rather different class of materials is the sulphate LiKSO_4 (San Karam *et al.*, 1989) (critical transformation pressure 12 GPa) which would suggest that a very wide range of materials may show pressure-induced amorphisation at relatively low temperatures. These examples have all been associated with change of coordination with increasing pressure, but there would appear to be no reason (where a reconstructive transition occurs) for amorphisation not to occur also on reducing pressure, provided the temperature is low enough. An example here is CaSiO_3 perovskite, stable only at very high pressures, e.g. above 1 GPa (Liu and Ringwood, 1975) reducing pressure the octahedral silicon becomes unstable and an amorphous tetrahedral solid is obtained.

In all these cases, and others resembling them, I believe recrystallisation will occur at relatively low temperatures ($\frac{1}{2} T_M$) so that it is unlikely in my view that such pressure-induced amorphisa-

tion will play a very significant role in geophysical/mechanical behaviour of rocks, e.g. in shear. The identification of amorphisation has, however, been developed to provide an extension to the coesite/stishovite-based techniques for detecting shock impact, e.g. by meteorites. The major problem here of course being the previously noted difficulty of detection of an amorphous material by standard techniques.

Glasses

We now come to true glasses—'true' is used to differentiate the full behaviour of a glassy solid from that of amorphous solids often styled 'glasses' (see above). The key feature that distinguishes a glass from other amorphous solids is that it shows a transformation region as temperature is increased in which its volume-dependent properties such as density, thermal expansion and refractive index, gradually change in temperature dependence from behaviour typical of a solid to that typical of a liquid, and in principle do so reversibly and indefinitely. At the nominal transition temperature, T_g , which can be at about two-thirds the melting point of the corresponding crystalline solid, viscosity is extremely high, above 10^{13} poise, but it falls continuously with increasing temperature and eventually, at a sufficiently high temperature, can reach typically liquid values of a few tenths of a poise. This transformation can usually be repeated indefinitely in pure systems, but the presence of impurities can induce crystallisation and suppress the prolonged reduction in viscosity towards low temperatures compared with crystalline solids. This behaviour of glass also shows a time dependence or, perhaps more correctly, a heating-or-cooling rate dependence. Thus the temperature of the inflection point of the characteristic transformation curve, defined as T_g , depends on the rate of cooling. At low rates the solid curve 'peels off' at a lower temperature than at high rates. However even at geological cooling rates there is no very significant depression of T_g since there is a log rate dependence.

Some years ago a heterodox model of the glassy state was put forward by this author (Goodman, 1985, 1986, 1987). The model is able to explain this behaviour. It also provides a new definition of a glass-former, that is of a material that can form glasses which of course would show the unusual temperature and rate dependent viscosity characteristics described above. Interestingly for a material to act in this way it has to form at least two polymorphs whose free energies differ but little (thus SiO_2 , for example, makes a good glass

former). Returning to the model, it is a phase-diagram-based approach and can also explain the curious fact that, as has been known for years but never understood, the compositions of the best glasses are associated with, though not exactly at, reasonably deep eutectics.

Since pressure induces polymorphism, and can also introduce new phases and new eutectics, one can argue in principle that complex mineral phase diagrams could develop glass-forming ability in eutectic regions at pressures close to some crystallographic transformation boundary, perhaps, for example, olivine-spinel in $(\text{Mg,Fe})_2\text{SiO}_4$. This is an entirely general argument and one not meant to be restricted in any way to the example quoted.

Why this kind of effect could be of geophysical importance is because rocks cooling from high temperature in an appropriate pressure range at an appropriate depth, would tend to segregate near-eutectic compositions to grain boundaries. There, should they form a glass, one will have a thin region of material round each grain of rock that will remain of low viscosity in a geological sense, e.g. of $\sim 10^{12}$ poise at a temperature approaching T_g for the glass—which is likely to be roughly $0.6 T_m$ for the corresponding eutectic. Such glassy films therefore, might allow enhanced creep in rocks enormously greater than might normally be expected for crystalline material. One restriction here could be devitrification, that is the crystallisation of the glass, which could be induced by some impurities—or suppressed by others. Clearly what is needed here is an investigation of glass formation under pressure, and, also, of stability against devitrification. The latter presents obvious practical difficulties if conceived in terms of a direct experimental verification (geological time-scales are long). What is needed is the development of techniques for the examination of actual rocks to check for the presence of glass at grain boundaries.

It must be stressed however that thin glassy films can readily be overlooked when studying mineralogical specimens by standard techniques. Their volume is small and their diffraction spectra diffuse so that very considerable care would need to be taken. It is more than likely that new techniques will need to be developed.

It is also worth pointing out perhaps, that generally it has been the high-pressure induced

phase transformations of relatively pure phases that have been investigated, e.g. in diamond anvil cells, and not the phase diagrams as a whole with their eutectics. One could perhaps ask the question: are eutectic temperatures even known in the key system $(\text{Fe,Mg})_2\text{SiO}_4$ – $(\text{Fe,Mg})\text{SiO}_3$ – SiO_2 in the pressure range 50 to 150 GPa? And if such eutectics are found what is the effect on them of geo-relevant impurities such as Al_2O_3 and TiO_2 ; do these form still deeper eutectics? These questions are important both because the eutectics in any case correspond to low melting compositions segregating to grain boundaries, but also because of the possibility outlined above that they could form true glasses showing significantly low viscosities to quite unexpectedly low temperatures.

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