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**SOLUBILITY AND STABILITY OF INORGANIC CARBONATES:
AN APPROACH TO THE SELECTION OF A WASTE FORM
FOR CARBON-14**

SOLUBILITE ET STABILITE DES CARBONATES INORGANIQUES:

UNE APPROCHE AU CHOIX D'UNE FORME DE DECHETS POUR LE CARBONE 14

Peter Taylor

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RÉSUMÉ

On examine la chimie des carbonates inorganiques tout en attachant de l'importance à la solubilité et stabilité hydrolytique pour identifier les formes de déchets à retenir pour l'immobilisation et l'évacuation du ^{14}C . À l'heure actuelle, CaCO_3 et BaCO_3 sont les deux formes de déchets généralement préférées, principalement du fait que ce sont les produits de la technologie éprouvée d'épuration du CO_2 . Elles ont toutefois une solubilité relativement élevée dans les solutions non alcaline et il faut donc apporter du soin à choisir et évaluer un milieu d'évacuation approprié. On identifie trois composés à meilleures propriétés de solubilité dans les eaux presque neutre, à savoir: la bismutite, $(\text{BiO})_2 \text{CO}_3$; l'hydro-cérussite, $\text{Pb}_3 (\text{OH})_2 (\text{CO}_3)_2$; et la rhodochrosite, MnCO_3 . On examine certaines des limites de chacune de ces autres formes possibles de déchets.

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ABSTRACT

The chemistry of inorganic carbonates is reviewed, with emphasis on solubility and hydrolytic stability, in order to identify candidate waste forms for immobilization and disposal of ^{14}C . At present, CaCO_3 and BaCO_3 are the two most widely favoured waste forms, primarily because they are the products of proven CO_2 -scrubbing technology. However, they have relatively high solubilities in non-alkaline solutions, necessitating care in selecting and assessing an appropriate disposal environment. Three compounds with better solubility characteristics in near-neutral waters are identified: bismutite, $(\text{BiO})_2\text{CO}_3$; hydrocerussite, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$; and rhodochrosite, MnCO_3 . Some of the limitations of each of these alternative waste forms are discussed.

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1. INTRODUCTION

Carbon-14 is a beta-emitting radioisotope with a half-life of 5730 years. It is produced by various neutron reactions in nuclear power reactors: $^{13}\text{C}(n,\gamma)^{14}\text{C}$, $^{14}\text{N}(n,p)^{14}\text{C}$, and $^{17}\text{O}(n,\alpha)^{14}\text{C}$. The third reaction, taking place in the heavy water moderator, is the most important source of ^{14}C in CANDU* reactors [Stasko and Vivian, 1983]. Lesser amounts are produced in the fuel and primary heat-transport system. The moderator reaction accounts for a disproportionately high contribution from CANDU reactors to world production of ^{14}C .

Scheele and Burger [1982] cite estimates of 0.6 and 2.0 MCi of ^{14}C produced in nuclear reactors world-wide by the year 2000. Stasko and Vivian [1983] estimated 0.04 MCi produced in Ontario Hydro reactors, and 0.2 MCi elsewhere, by 1995. The global natural inventory and production rate (mainly from cosmic irradiation of nitrogen in the upper atmosphere) are about 300 MCi and 38 kCi/yr, respectively [Stasko and Vivian, 1983]. (1MCi = 0.74 tonnes of $^{14}\text{CO}_2$).

The need to control release of man-made ^{14}C to the environment has been recognized, and Scheele and Burger [1982] have reviewed some candidate waste forms. They concluded that the most suitable materials are calcium, barium, and strontium carbonates in concrete, the calcium carbonate concrete being slightly superior to the others. Barium and calcium carbonates are also products of $^{14}\text{CO}_2$ immobilization processes. They are relatively soluble, however, in non-alkaline solutions (pH < 10).

The report by Scheele and Burger [1982] includes some discussion of the solubility and thermal stability of several inorganic carbonates. This report presents a more detailed analysis of solubility and stability relationships, with a view to identifying other candidate waste forms for ^{14}C , with particular attention to materials that are stable and relatively insoluble in near-neutral aqueous solutions. Other selection criteria, such as economic and other practical considerations, are not addressed, apart from noting where chemical toxicity of a material is an obvious concern. Given the small mass of carbon involved, material costs are unlikely to be a determining factor in waste-form selection, unless the ^{14}C is isotopically diluted before immobilization.

The carbonates of all stable elements, plus uranium and thorium, are discussed in the following sequence:

- (1) Alkali metals
- (2) Alkaline earths
- (3) Remaining main-group elements
- (4) First-row transition metals, Ti to Zn
- (5) Second- and third-row transition metals,
Zr to Cd and Hf to Hg
- (6) Lanthanides, actinides, scandium and yttrium.

* CANada Deuterium Uranium

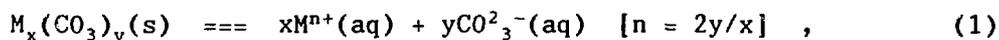
Mixed carbonates, i.e. carbonates of more than one metal, are only discussed when they may affect the stability of a compound under discussion. Similarly, complex salts containing anions other than CO_3^{2-} , HCO_3^- , O^{2-} and OH^- are not discussed in general, although some specific examples are mentioned. This report does not consider reduced carbon waste-forms, such as graphite, metal carbides, or organic materials.

2. GENERAL CONSIDERATIONS

Many metals form carbonate salts; for a brief review of their general chemistry, see Holliday et al. (1973). Carbonates may be regarded as the products of reaction between CO_2 and basic oxides, or the combination of metal cations and carbonate anions. These two definitions lead to distinct, but complementary, descriptions of the stability and solubility of a solid carbonate.

2.1 THE SOLUBILITY OF A CARBONATE

A general expression of the solubility of a solid carbonate is equilibrium (1):



for which the equilibrium constant is given by equation (2)

$$\log K_{sp} = x \log\{\text{M}^{n+}\} + y \log\{\text{CO}_3^{2-}\}^* \quad . \quad (2)$$

If congruent dissolution occurs in accordance with equation (1), then:

$$[\text{M}^{n+}] = (x/y)[\text{CO}_3^{2-}] \quad (3)$$

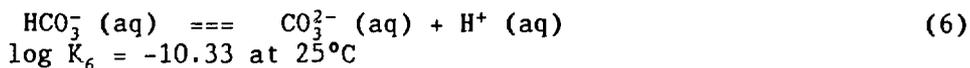
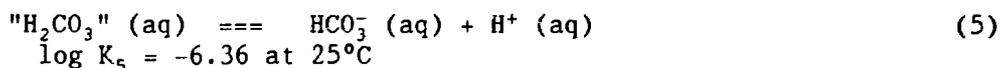
Substituting this expression into equation (2), and rearranging, we obtain:

$$\log[\text{CO}_3^{2-}] = \frac{\log K_{sp} - x \log(x/y)}{(x+y)} \quad . \quad (4)$$

These expressions are of limited use, however, since they only describe total dissolved metal and carbonate concentrations in a few situations - at $\text{pH} > 11$, and only with cations that are not hydrolyzed or complexed to a significant extent. Nonetheless, if Gibbs energies of formation, $\Delta_f G^\circ$, are known for the solid and for aqueous M^{n+} and CO_3^{2-} , this does provide a basis for preliminary comparison of the solubilities of different solids. In particular, it gives us a lower limit of solubility, which is useful for ruling out solid carbonates that are obviously too soluble to be considered as ^{14}C waste forms.

* The term $\{X\}$ represents the chemical activity of species X in solution. In dilute solutions (ionic strength less than $0.01 \text{ mol}\cdot\text{dm}^{-3}$), this closely approximates to the concentration of the species, $[X]$. In the following discussion, activities are strictly expressed as molalities, i.e. moles per kilogram of water. These are not significantly different from molarities ($\text{mol}\cdot\text{dm}^{-3}$) in the present context.

Carbonate speciation in water is governed by the carbonic acid[‡] dissociation equilibria:



Thus, at $\text{pH} < 11$, CO_3^{2-} represents only a fraction of the total dissolved carbonate, C_t , according to equation (7):

$$\{C_t\} = \{\text{CO}_3^{2-}\} \left(1 + \frac{\{\text{H}^+\}}{K_6} + \frac{\{\text{H}^+\}^2}{K_5 K_6} \right) \quad (7)$$

Consequently, the solubility of a metal carbonate generally increases with decreasing pH (below 11), since sufficient carbonate must be supplied to satisfy equilibria (5) and (6) as well as (1). (This trend may be reversed by the added effects of cation hydrolysis, described below). Figure 1 illustrates this effect for two cases, with control of metal concentration by dissolution of the carbonate, or by other factors.

Most metal cations, M^{n+} , with $n > 1$, undergo hydrolysis reactions to form hydroxo complexes of the type $\text{M}(\text{OH})_m^{-m+n}$, and sometimes also polymeric species, in non-acidic solutions [Baes and Mesmer, 1976]. In such cases, the total dissolved metal activity, $\{\text{M}_t\}$, can greatly exceed the activity of M^{n+} alone. The effect on carbonate solubility is to raise it to much higher levels than those indicated by the simple solubility product in expressions (1) to (4) above.

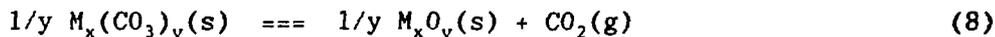
A full description of the solubility of a metal carbonate as a function of pH may thus be very complex. It may be complicated further if soluble metal carbonate complexes are also formed. Nonetheless, such a description is possible if the metal speciation and solid interconversion equilibria (see below) are sufficiently well characterized. An example, the lead carbonate system, is described by Taylor and Lopata [1984].

A recent study of carbonate titrations has revealed another anion, probably $\text{H}_3\text{C}_2\text{O}_6^-$, which contributes to carbonate speciation in moderately concentrated solutions (above about $10^{-4} \text{ mol}\cdot\text{dm}^{-3}$) near pH 7 [Covington, 1985]. This species has not been taken into account in the following discussion. It is expected to cause a small increase in solubilities near pH 7.

[‡]"Carbonic acid" consists largely of dissolved CO_2 , as opposed to H_2CO_3 . For equilibrium calculations and other thermodynamic purposes, the two species are commonly lumped together as " H_2CO_3 ".

2.2 EQUILIBRIA INVOLVING TWO SOLIDS

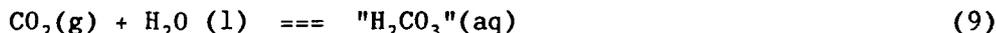
At first sight, the addition of a second solid to the solubility equilibrium seems likely to complicate matters still further. However, certain aspects may be greatly simplified if the second solid is an oxide, hydroxide or basic carbonate that, together with the first solid, buffers the dissolved carbonate. This buffering can be expressed in a variety of ways, of which the simplest is probably equation (8):



$$K_8 = p(CO_2)$$

If the second solid is a hydroxide or a basic carbonate, the equilibrium may involve water, but in dilute aqueous systems the equilibrium constant still reduces simply to a CO_2 partial pressure (strictly fugacity), which is easily determined if $\Delta_f G^\circ$ values are available for both solids.

The total free carbonate activity is related to $p(CO_2)$ by equations (6), (7) and (9):



$$K_9 = {"H_2CO_3"} / p(CO_2) = 10^{-6.46} \text{ mol} \cdot \text{kg}^{-1} \cdot \text{Pa}^{-1}$$

whence:

$$\{C_t\} = K_9 p(CO_2) \left(1 + \frac{K_5}{\{H^+\}} + \frac{K_5 K_6}{\{H^+\}^2} \right) \quad (10)$$

The form of this expression is shown in Figure 2. Note that, when $p(CO_2)$ is fixed, $\{C_t\}$ decreases (to a limiting value) with decreasing pH, whereas it increases with decreasing pH when $\{CO_3^{2-}\}$ is fixed.

In equilibrium (8), we thus have a situation in which the equilibrium total carbonate activity is independent of metal hydrolysis, although metal carbonate complexes might still contribute significantly to the total. As long as the solution is saturated with respect to both materials, the two solids in combination will buffer $p(CO_2)$ at a value equal to K_8 . However, if the prevailing $p(CO_2)$ in the solution is less than K_8 , then the carbonate is unstable. The only limitations on this situation are that the two solids must coexist in equilibrium under the stated conditions of pH and solution composition. Thus, for example, $PbCO_3$ and PbO would not be an appropriate choice of solids because this combination is unstable in water with respect to formation of the two basic carbonates, $Pb_3(OH)_2(CO_3)_2$ and $Pb_{10}O(OH)_6(CO_3)_6$, [Taylor and Lopata, 1984]. Also, PbO can exist as an equilibrium phase only within the pH range from about 8 to 14. Outside these limits, calculated solubilities of PbO exceed physically meaningful values. In practice, lead solubilities are then determined by other solids. This range of pH may be limited further by reaction with other ions.

An alternative description of equilibrium (8) is that, according to the phase rule, the phase assemblage [carbonate + oxide + solution] has only one degree of freedom in the system [M_xO_y - CO_2 - H_2O -(pH)] at a given temperature and total pressure. Here, the notation (pH) indicates that the pH is adjusted by a non-interacting acid or base. In comparison, the assemblage [carbonate + solution] has two degrees of freedom, and is therefore more difficult both to describe and to control.

In the following general survey of inorganic carbonates (Section 3), two criteria, based on equilibria of types (1) and (8), are used to determine which solids show some promise as waste forms for ^{14}C .

- (a) Any carbonate for which $\log[CO_3^{2-}] > -3$, as determined using equations (1) to (4), is dismissed as too soluble for further consideration, since it is at least an order of magnitude more soluble than $CaCO_3$.
- (b) Any carbonate for which $p(CO_2)$, as defined by a reaction such as (8), exceeds 0.1 Pa, is dismissed as too unstable for further consideration. This eliminates solids that are unstable, or only marginally stable, under ambient conditions ($p(CO_2) \approx 30$ Pa in air). Although it is used here as a measure of hydrolytic stability, K_8 is also an approximate measure of relative thermal stability.

These criteria are not based on any radiological considerations. They simply provide a self-consistent method to identify carbonates that are sufficiently insoluble and stable to justify further evaluation as candidate waste forms for ^{14}C . The thermodynamic database used for this selection is given in Tables 1 to 9, and discussed in Section 4.

For those carbonates that meet these two criteria, a more detailed chemical discussion is presented, covering aspects including metal ion hydrolysis and complexation, redox reactions, thermal stability, interactions with other ions and metal toxicity.

Unless otherwise stated, the following discussions refer to standard conditions of 10^5 Pa total pressure and a temperature of $25^\circ C$.

3. SURVEY OF INORGANIC CARBONATES

The following discussion draws heavily from the 1973 treatise on inorganic chemistry by Bailar et al., and from thermodynamic data compilations by Robie et al. [1979] and Wagman et al. [1982]. For more detailed information on the chemistry and mineralogy of carbonates, with emphasis on calcium and magnesium compounds, refer to Lippman [1973] and Chilingar et al. [1967]. Palmer and van Eldik [1983] is a useful source of information on some of the less common inorganic carbonates.

3.1 ALKALI METALS (Li,Na,K,Rb,Cs)

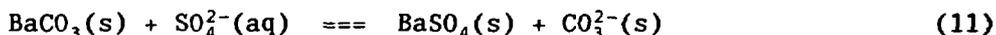
Since the alkali metal oxides and hydroxides are very strong bases, the alkali metal carbonates are expected to be very stable. The alkali metals do indeed form a variety of solid carbonates and bicarbonates, including hydrates and double salts [Whaley, 1973]. However,

all of these compounds are moderately to highly soluble. The least soluble of all, Li_2CO_3 , has a solubility of about $0.18 \text{ mol}\cdot\text{dm}^{-3}$ at 25°C [Hart and Beumel, 1973]. These compounds can therefore be dismissed immediately as ^{14}C waste forms.

3.2 ALKALINE EARTH ELEMENTS (Be, Mg, Ca, Sr, Ba)

The carbonates of these elements include the two most commonly proposed waste forms for ^{14}C : CaCO_3 and BaCO_3 [Scheele and Burger, 1982]. Since Be and Mg both form basic carbonates as well as "simple" carbonates, they are discussed separately from Ca, Sr and Ba.

The solubilities of CaCO_3 , SrCO_3 and BaCO_3 are reasonably well described by equations (1) to (4) because aqueous Ca^{2+} , Sr^{2+} and Ba^{2+} are not strongly hydrolyzed or complexed in aqueous carbonate solutions. All three compounds have $\log K_{sp}$ values near -9, so they meet the first criterion. All three also easily meet the criterion of stability. However, the high solubilities of the hydroxides preclude the possibility of buffering $p(\text{CO}_2)$ with the phase assemblages $\text{M}(\text{OH})_2 + \text{MCO}_3$, in the manner described in Section 2.2. The performance of the alkaline earth carbonates as ^{14}C waste forms is therefore strictly limited by the increase in solubility as the pH decreases below about 11, as shown in Figure 3. (This may not be a problem if pH is controlled near 11 by a concrete matrix). Although SrCO_3 and BaCO_3 are somewhat less soluble than CaCO_3 , the much greater abundance of Ca in groundwaters and minerals tends to favour CaCO_3 as a waste form, since it should be possible to select a disposal site in which the groundwater is already saturated with CaCO_3 . The high natural abundance of calcium also raises the concern that BaCO_3 or SrCO_3 may be altered to CaCO_3 , allowing release of ^{14}C by exchange of carbonate with the groundwater. Also, the low solubility of BaSO_4 would promote alteration of BaCO_3 in sulfate-containing groundwaters:



$$K_{11} = \{\text{CO}_3^{2-}\} / \{\text{SO}_4^{2-}\}$$

The value $\log K_{11} = +1.4$ is much higher than corresponding values of -2.8 and -3.9 for the strontium and calcium systems, respectively (the calcium value refers to gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, rather than anhydrous CaSO_4).

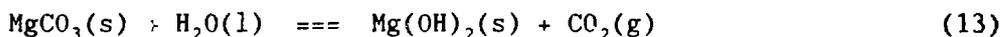
Disposal of $\text{Ca}^{14}\text{CO}_3$ in a site containing calcite-saturated groundwaters may thus be acceptable, if the disposal of other wastes in the vicinity does not cause significant thermal or chemical disruption of the groundwater. Some attention may be needed to assess the importance of isotopic exchange (reaction 12), as a mechanism for release of ^{14}C :



where $(\text{CO}_3)_{sp}$ denotes whatever dissolved carbonate species are involved. It may also be necessary to assure that the waste material is calcite, rather than one of the metastable forms of calcium carbonate (aragonite, vaterite, or $\text{CaCO}_3\cdot\text{H}_2\text{O}$). In groundwaters rich in other multivalent cations, it is also possible for alteration reactions to occur, since CaCO_3 forms a wide variety of double carbonates, some of which are mentioned in the following discussion.

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The magnesium carbonate system is much more complicated than the Ca, Sr or Ba systems, since it involves a variety of basic and hydrated carbonates as well as magnesite (MgCO_3). Lippmann [1973] has discussed the phase relationships in this system at some length. He concludes that MgCO_3 is the only stable solid carbonate of magnesium under conditions near ambient, but that hydrated or basic compounds often precipitate metastably. Even MgCO_3 is only stable at $p(\text{CO}_2) > 10^{-1.2}$ Pa, thus meeting our stability criterion by a very narrow margin:



$$K_{13} = p(\text{CO}_2) = 10^{-1.2} \text{ Pa}$$

We therefore rule out the magnesium carbonates as candidate waste forms for ^{14}C .

Beryllium carbonates have been reviewed briefly by Everest [1973]. They can probably be ruled out on the grounds of beryllium toxicity alone, but there also appears to be no chemical reason for selecting a beryllium carbonate waste form. The hydrated carbonate, $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$ is stable only under an atmosphere of CO_2 , indicating that its decomposition partial pressure is high. Beryllium also forms some ill-defined basic carbonates, but they do not appear to be especially stable. There is also some indication that beryllium forms some soluble carbonate complexes [Sengupta, 1964].

3.3 OTHER MAIN-GROUP (p-BLOCK) ELEMENTS

Only a few of these elements form carbonate salts; most of them are too electronegative to form stable cations in aqueous solution, and/or they form acidic oxides, which do not combine with CO_2 . Thus, those elements in the periodic table that lie on or to the right of a diagonal line from boron to tellurium, inclusive, can be eliminated from further consideration. However, some of the heavier elements in groups III, IV and V do form salts and basic salts, including a few carbonates. The most important compounds in the present context are the basic carbonates of lead(II) and bismuth(III), which are discussed in detail at the end of this section. All elements heavier than bismuth are radioactive.

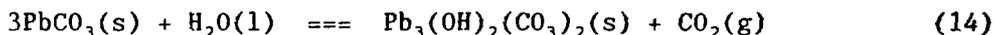
Aluminum has been reported to form some ill-defined basic carbonates, but there is no indication that they are particularly stable [Wade and Banister, 1973a]. The best-known carbonate of aluminum appears to be the mineral dawsonite, which is a double salt, $\text{NaAl}(\text{OH})_2\text{CO}_3$; Gibbs energy data given by Robie et al. [1979] indicate that it is only marginally stable under ambient conditions. Several complex carbonate minerals of aluminum, strontium and barium have been reported recently [Roberts et al., 1986, and references therein]. Their stability relationships are unknown, but they are unlikely to prove more attractive than SrCO_3 or BaCO_3 as ^{14}C waste forms.

It is possible that a framework aluminosilicate, such as sodalite, could accommodate carbonate ions. Such a material might have sufficient kinetic stability to justify being selected as a waste form, but would almost certainly not meet the thermodynamic criteria used in this discussion. A similar approach to the immobilization of ^{129}I in iodide-sodalite shows considerable promise [Vance et al., 1981; Dunn et al., 1985].

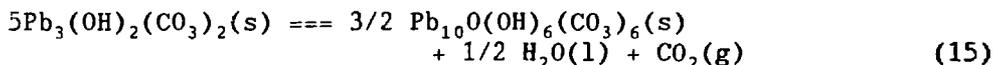
There is no indication that either gallium or indium form stable carbonates [Wade and Banister, 1973b]. Tin and antimony form a variety of both simple and basic salts, but there are apparently no authenticated reports of carbonates [Abel, 1973; Smith, 1973]. Although tin and antimony carbonates may well exist, they are unlikely to be as stable as the lead and bismuth compounds, described below. Thallium(I) carbonate, like the alkali metal carbonates, is quite stable, but too soluble to be considered ($> 0.1 \text{ mol}\cdot\text{dm}^{-3}$ [Wade and Banister, 1973c]). Thallium is also very toxic.

Stability limits of lead and bismuth carbonates were determined recently in some detail [Taylor and Lopata, 1984; Taylor, Sunder and Lopata, 1984]. That work was prompted by the possible use of PbO or Bi_2O_3 to remove ^{14}C from CANDU moderator systems. Reaction kinetics proved to be too slow for this application, but some of the solids still show some promise as ^{14}C waste forms.

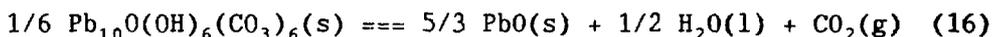
In the lead system, the solubility and stability limits of PbO (litharge), $\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6$ (plumbonacrite), $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ (hydrocerussite) and PbCO_3 (cerussite) in the system $\text{PbO}-\text{CO}_2-\text{H}_2\text{O}-(\text{pH})$ were determined at 25°C . Equilibria between these solids can be described by equations of the same type as (8), as follows:



$$K_{14} = p(\text{CO}_2) = 13 \pm 2 \text{ Pa}$$



$$K_{15} = p(\text{CO}_2) = 10^{-2.9 \pm 1.6} \text{ Pa}$$



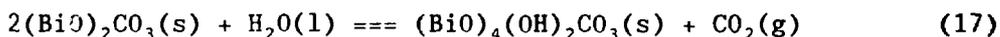
$$K_{16} = p(\text{CO}_2) = 10^{-4.9 \pm 0.6} \text{ Pa}$$

The high value of K_{14} shows that PbCO_3 can be dismissed as a ^{14}C waste form because of its instability with respect to hydrolysis to hydrocerussite (reaction (14)). The low value of K_{16} suggests that [litharge + plumbonacrite] might be an appropriate waste form. However, plumbonacrite is only stable over a narrow range of $p(\text{CO}_2)$, between K_{16} and K_{15} , and reaction to form hydrocerussite would be expected in carbonate-containing groundwaters. Although the solubilities of these two basic carbonates are very similar (see Figure 5 in Taylor and Lopata, 1984), this reaction might provide a facile route for ^{14}C release by isotopic exchange.

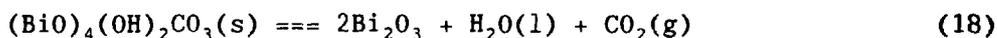
The prediction that plumbonacrite would convert to hydrocerussite is supported by the relative abundance of hydrocerussite, and scarcity of plumbonacrite, in nature. The high solubility of PbO, and the toxicity of lead, give further reason not to choose [litharge + plumbonacrite] as a waste form.

The solubility/stability relationships between PbO and the lead carbonates are illustrated in Figure 4. Hydrocerussite solubility shows a broad minimum of about 10^{-6} mol·dm⁻³ total lead, around pH = 9.5 and $\{C_T\} = 10^{-4}$ mol·dm⁻³. These values also lie near the centre of the stability field (Figure 4), with respect to conversion to other carbonates. If such groundwater chemistry could be sustained in a repository environment, then hydrocerussite might be an appropriate waste form. The interconversion of cerussite and hydrocerussite is readily reversible, with $K_{14} = 13$ Pa [Taylor and Lopata, 1984]. Since this value is very close to the atmospheric partial pressure of CO₂ (~ 30 Pa), hydrocerussite would not be an appropriate ¹⁴C waste form for shallow burial. It is unlikely that any groundwaters would be sufficiently alkaline or deficient in carbonate to alter hydrocerussite to plumbonacrite. Alteration to PbS, PbSO₄ or basic lead sulfates, might be a problem in sulfur-containing groundwaters, and alteration to elemental lead is possible under strongly reducing conditions [Garrels and Christ, 1965, pp. 233-238].

There are some similarities between the lead(II) and bismuth(III) carbonate systems, in that there are two basic bismuth carbonates [Taylor et al., 1984]. However, the binary carbonate, Bi₂(CO₃)₃, is unknown, and is probably not stable under normal conditions. Equilibria in this system at 25°C are described by equations (17) and (18).



$$K_{17} = p(\text{CO}_2) = 10^{-4.4 \pm 1.0} \text{ Pa}$$

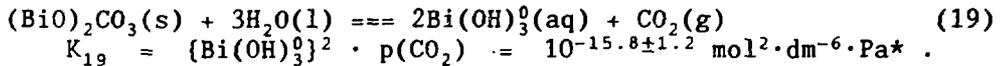


$$K_{18} = p(\text{CO}_2) = 10^{-5.5 \pm 1.0} \text{ Pa}$$

The intermediate carbonate, (BiO)₄(OH)₂CO₃, is only stable over a very narrow range of p(CO₂), between K₁₇ and K₁₈. At p(CO₂) < K₁₈ or pCO₂ > K₁₇, it is unstable with respect to α-Bi₂O₃ (bismite) and (BiO)₂CO₃ (bismutite), respectively. It is therefore not favoured as a waste-form component, for the same reasons as plumbonacrite, even though it would tend to buffer p(CO₂), and hence carbonate activities, at very low values.

The wide stability field of (BiO)₂CO₃, compared with hydrocerussite, makes it an appealing choice as a ¹⁴C waste form. This is supported by the common occurrence of bismutite in oxidized bismuth ores [Fron del, 1943; Sahama and Lehtinen, 1968]. In addition, bismuth is much less toxic, and generally rather less soluble, than lead. Unfortunately, the aqueous solution chemistry of bismuth(III) is complex, and less completely understood than that of lead(II). However, the neutral species, Bi(OH)₃⁰, is believed to predominate in neutral to moderately alkaline solutions [Bidleman, 1971; Baes and Mesmer, 1976, p. 382]. The solubility

of $(\text{BiO})_2\text{CO}_3$ in such solutions may therefore be dominated by equilibrium (19):



Dissolved bismuth activities, based on this equilibrium, as a function of pH and total free carbonate activity, are shown in Figure 5. Assuming no contribution from bismuth carbonate complexes (and these cannot be completely ruled out), this should be a reasonable description of $(\text{BiO})_2\text{CO}_3$ solubility within the pH range from about 6 to 13. At $\text{pH} > 12.5$, $\text{Bi}(\text{OH})_4^-$ becomes important, and at $\text{pH} < 6$ the solubility increases rapidly because of the formation of polymeric hydroxybismuth cations [Baes and Mesmer, 1976, pp. 375-383]. Note that hydrolysis to $(\text{BiO})_4(\text{OH})_2\text{CO}_3$ or Bi_2O_3 can also occur at high pH and low carbonate activity. The very low dissolved bismuth activities under normal groundwater conditions ($\text{pH} = 6 - 10$, $pC_t = 2-4$) indicate that a $(\text{BiO})_2\text{CO}_3$ waste form should be chemically durable. Alteration to other basic bismuth salts is not expected, with the possible exception of beyerite, $\text{Ca}(\text{BiO})_2(\text{CO}_3)_2$, which may be stable in calcite-saturated waters [Fron del, 1943; Chaundy et al., 1969]. As with lead carbonates, bismuth carbonate is unstable with respect to elemental bismuth under strongly reducing conditions, and formation of Bi_2S_3 is possible in reducing, sulfur-containing waters. Alteration to solid sulfates appears not to be a major concern in either the lead or bismuth system, although some caution is needed here in view of the complex basic salt chemistry of both elements. Alteration of $(\text{BiO})_2\text{CO}_3$ to BiOCl or other basic bismuth chlorides can occur in acidic, concentrated chloride solutions.

3.4 FIRST-ROW TRANSITION METALS (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn)

The only carbonates of these elements are simple and, in some cases, basic or hydrated carbonates of the divalent elements from Mn to Zn. The absence of carbonates of trivalent and tetravalent metals (e.g. Fe^{3+} , Ti^{4+}) is probably due to the high lattice energies of the corresponding oxides and, hence, high decomposition pressures for the hypothetical carbonates. (TiO_2 , however, is a component of the complex carbonate mineral sabinaitite [Jambor et al., 1980; Chao and Jiexiang, 1985]). The small number of higher-valent oxides (e.g. V_2O_5 , CrO_3 , Mn_2O_7) are all strongly acidic, and so are not expected to combine with CO_2 . Chromium(II) carbonate might be expected to exist, but only under strongly reducing conditions. There are some vague references to copper(I) carbonate, but it appears to be ephemeral, if it exists at all.

*The uncertainty in K_{19} is based on $p(\text{CO}_2) = 10^{-5.0 \pm 1.0} \text{ Pa}$ for $(\text{BiO})_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Bi}_2\text{O}_3(\text{s}) + \text{CO}_2(\text{g})$ (derived from Taylor et al. [1984]), and $K = 10^{-5.4 \pm 0.1}$ for $1/2 \text{ Bi}_2\text{O}_3(\text{s}) + 3/2 \text{ H}_2\text{O}(\text{l}) \rightleftharpoons \text{Bi}(\text{OH})_3^0(\text{aq})$, from Baes and Mesmer [1976], after Bidleman [1971].

All of the MCO_3 compounds in this series have relatively low solubility products, ($\log K_{sp} \sim -10$, see Table 9) and thus meet the first criterion discussed at the end of Section 2.2. However, high decomposition pressures rule out all but MnCO_3 , and possibly also CoCO_3 , from further consideration (Section 4). The solubility product of MnCO_3 is about two orders of magnitude lower than that of CaCO_3 . However, the comparison between manganese and calcium carbonates is complicated by both the hydrolysis of manganese(II) in solution and the diverse redox chemistry of manganese.

The computed solubilities and stability fields of MnCO_3 and CaCO_3 , and the two hydroxides, are compared in Figure 6. The figure shows dissolved manganese and calcium activities in equilibrium with solutions having total free carbonate activities of 10^{-2} , 10^{-4} and $10^{-6} \text{ mol}\cdot\text{kg}^{-1}$, as a function of pH. Manganese carbonate appears to be substantially less soluble than CaCO_3 under the neutral to slightly alkaline conditions expected to prevail in a waste vault. Conversion to Mn(OH)_2 is expected only in strongly alkaline or carbonate-deficient waters.

Some aspects of the thermodynamic database would need further refinement before a case could be made to adopt MnCO_3 as a ^{14}C waste form. In particular, the differences in stability between well-crystallized and "active" precipitated samples of Mn(OH)_2 and MnCO_3 need to be taken into account, as outlined in Section 4.4. In addition, Baes and Mesmer [1976, pp. 221-223] state that the experimental data for Mn^{2+} hydrolysis equilibria are not completely satisfactory. A recent review by Chiswell and Mokhtar [1986] indicates that many uncertainties persist about the speciation of manganese(II) in natural waters.

The stability of MnCO_3 with respect to higher oxides of manganese also needs to be considered. The effect of oxidation on equilibrium CO_2 pressures is illustrated in Figure 7. The phase assemblage ($\text{Mn(OH)}_2 + \text{MnCO}_3$) is only stable under reducing conditions, but the ($\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$) redox buffer lies well within the Mn(OH)_2 stability field. This fact, and the fairly widespread natural occurrence of rhodochrosite, indicates that a satisfactory environment for disposal of $\text{Mn}^{14}\text{CO}_3$ should not be too difficult to attain. We therefore retain MnCO_3 on the "short list" of candidate waste forms for ^{14}C . Other reactions that may need to be taken into account in assessing MnCO_3 include the formation of MnS and $\text{CaMn(CO}_3)_2$ [Rosenberg and Foit, 1979].

Nickel and cobalt have both been reported to form hydrated carbonates, $\text{MCO}_3\cdot 6\text{H}_2\text{O}$ and also ill-defined basic carbonates. There is no indication that these are especially stable [Nicholls, 1973a and 1973b; Henmi et al, 1986]. A hydrated sodium nickel carbonate mineral, kambaldaite ($\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6\cdot 6\text{H}_2\text{O}$) has been reported recently [Nickel and Robinson, 1985]; its limited occurrence implies marginal stability.

The basic carbonates of zinc and copper are better understood than those of nickel and cobalt. Copper forms two such compounds: malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) and azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$). Although both occur in nature, they appear to be stable only near or above ambient CO_2 fugacities (Section 4). Recent investigations of the stability of malachite and azurite by [Woods and Garrels, 1986a and 1986b] appear to be definitive.

The basic zinc carbonate, hydrozincite ($Zn_5(OH)_6(CO_3)_2$) appears to be more stable than the copper compounds [Alwan and Williams, 1979; Neczaj-Hruzewicz et al., 1977], but does not quite meet our criterion for stability, stated in Section 2.2. Thus, we cannot make a case for any of these compounds as ^{14}C waste forms. Zinc and copper also form two mixed basic carbonates, aurichalcite ($(Zn,Cu)_5(OH)_6(CO_3)_2$) and rosasite ($(Cu,Zn)_2(CO_3)(OH)_2$); these are only marginally more stable than the individual copper and zinc carbonate minerals [Alwan et al., 1980].

3.5 SECOND- AND THIRD-ROW TRANSITION METALS (Zr to Cd and Hf to Hg)

Very few carbonates are known for these groups of elements, probably because most of the oxides are either highly refractory (e.g. ZrO_2), or acidic (e.g. MoO_3), or the metals are noble (e.g. Au, Pt). The only compound in this group that shows any promise as a ^{14}C waste form is cadmium carbonate (otavite, $CdCO_3$). It is somewhat less soluble, but also slightly less stable, than $MnCO_3$. However, the high toxicity of cadmium rules it out of serious consideration.

Similarly, mercury carbonates can probably be ruled out on toxicological grounds alone. They also do not show any special promise on chemical grounds. Mercurous carbonate, Hg_2CO_3 , is reported to decompose, with evolution of CO_2 , above $130^\circ C$ [Aylett, 1973a]. There are conflicting reports on mercuric carbonate. Some thermodynamic data indicate that it meets our criteria for solubility and (by a narrow margin) stability (see Section 4). However, other sources assert that there is no evidence for the existence of $HgCO_3$, and that efforts to prepare it result in HgO or ill-defined basic carbonates such as $Hg_4O_3CO_3$ [Aylett, 1973b].

A basic zirconium carbonate, $ZrCO_3 \cdot 2H_2O$, has been reported from a high-pressure synthesis by Ehrhardt et al. [1980]. Its stability is not known, but it seems unlikely to be stable at low CO_2 fugacities. Various basic carbonate salts, such as $K_6[Zr_2(OH)_2(CO_3)_6(H_2O)_6]$, are also known [Bradley and Thornton, 1973], as are a number of rare, complex zirconium carbonate minerals [Sabina et al., 1968; Jambor et al., 1980; Chao and Jiexiang, 1985; see also references cited by Roberts et al., 1986]. Similar compounds of other transition metals, especially Hf and Mo(IV), seem likely to exist, but they are unlikely to be of importance from a ^{14}C immobilization standpoint. Of the platinum metals, palladium seems most likely to form a carbonate ($PdCO_3$), but it is unlikely to be more than marginally stable under ambient conditions.

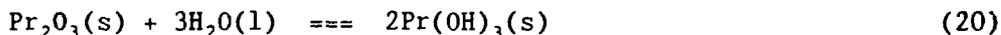
Finally, silver(I) carbonate, Ag_2CO_3 , is much less soluble than the other univalent metal carbonates (i.e. the alkali metals and thallium(I)). However, its decomposition pressure of CO_2 is too high to meet our stability criterion [Thompson, 1973].

3.6 LANTHANIDES, ACTINIDES, SCANDIUM AND YTTRIUM

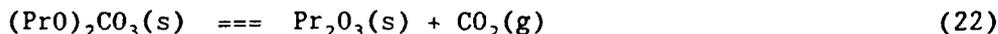
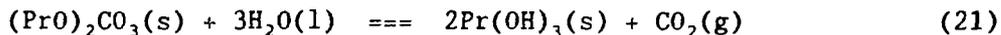
The lanthanide carbonate systems, $Ln_2O_3-CO_2-H_2O$, are complex and incompletely understood. About a dozen different solid compositions have been reported in these systems, and at least two of these ($Ln(OH)CO_3$ and $(LnO)_2CO_3$) are polymorphic [Kutty et al., 1985, and references therein]. Several rare-earth carbonate minerals are known; most of them contain other components, such as alkaline earths or fluoride [Felsche and Herrmann,

1978]. Bastnesite (or bastnaesite), $(\text{Ce},\text{La})(\text{CO}_3)\text{F}$, is an abundant mineral, and is isotypic with one of the forms of $\text{Ln}(\text{OH})\text{CO}_3$.

Firsching and Mohammadzadel [1986] have recently reported very low solubilities (10^{-7} to 10^{-8} $\text{mol}\cdot\text{dm}^{-3}$) for the rare-earth carbonates, $\text{Ln}_2(\text{CO}_3)_3$, but these compounds are readily hydrolysed to the hydroxycarbonates, $\text{Ln}(\text{OH})\text{CO}_3$ [Sun et al., 1986]. The oxycarbonates, $(\text{LnO})_2\text{CO}_3$ have very high thermal stability; the most stable, $(\text{LaO})_2\text{CO}_3$, decomposes to La_2O_3 only above 900°C , so its ambient decomposition partial pressure must be exceedingly low [Turcotte et al., 1969]. However, these compounds are much less stable with respect to hydration, hydrolysis, or both. For example, $\Delta_r G^\circ$ for reaction (20) is -137.2 $\text{kJ}\cdot\text{mol}^{-1}$ (see Table 4):



It follows that the decomposition partial pressure of CO_2 for reaction (21) will be about 24 orders of magnitude higher than for reaction (22):

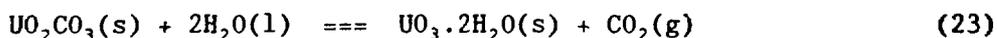


The hydroxycarbonates, $\text{Ln}(\text{OH})\text{CO}_3$, are presumably more stable than the oxycarbonates, $(\text{LnO})_2\text{CO}_3$, in low-temperature water.

The complexity of the lanthanide carbonate systems contrasts with the relative simplicity of the bismuth carbonate system. In particular, $(\text{BiO})_2\text{CO}_3$ is not prone to hydration or further carbonation, and is only hydrolysed in strongly alkaline solutions (or very dilute carbonate solutions). More detailed understanding of lanthanide carbonate phase relationships is needed, however before their possible use as ^{14}C waste forms can be properly assessed. The abundance of bastnaesite in nature suggests that $\text{Ln}(\text{OH},\text{F})\text{CO}_3$ compounds are the most promising candidate materials in these systems.

Scandium and yttrium are not lanthanide elements, but yttrium has a chemistry closely akin to the lanthanides, while scandium's chemistry is intermediate in nature between aluminum and the lanthanides. According to Vickery [1973], neither $\text{Y}(\text{OH})_3$ nor $\text{Sc}(\text{OH})_3$ reacts with atmospheric CO_2 , unlike $\text{La}(\text{OH})_3$. This strongly suggests that any carbonates of Sc and Y are stable (with respect to the hydroxides) only at relatively high CO_2 pressures. Scandium is known to form solid double carbonates such as $\text{Na}_5\text{Sc}(\text{CO}_3)_4$, but such compounds are sensitive to hydrolysis. The chemistry of a number of complex carbonates of scandium is reviewed by Palmer and van Eldik (1983). There is thus no indication that Sc or Y carbonates have any virtue as ^{14}C waste forms.

The two naturally occurring actinides, uranium and thorium, both form carbonates of limited stability. Rutherfordine, UO_2CO_3 , is quite insoluble, but appears to be only marginally stable under ambient conditions [Lemire and Tremaine, 1980]:



$$K_{23} = p(\text{CO}_2) = 2.7 \text{ kPa} [\log K_{23} = -1.6 \pm 0.8] .$$

A hydrated thorium carbonate, identified as $\text{Th}(\text{CO}_3)_2 \cdot 0.5 \text{H}_2\text{O}$, has been prepared at high CO_2 pressures, but is unlikely to be stable under ambient conditions [Ehrhardt et al., 1980]. The remaining actinides are themselves too great a radiological hazard for their carbonates to deserve consideration for ^{14}C immobilization.

4. THERMODYNAMIC INFORMATION ON INORGANIC CARBONATES

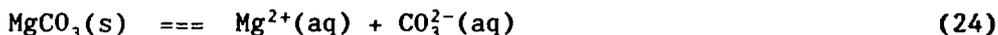
This section gives more detailed information supporting the statements about stabilities and solubilities of carbonates in Section 3. Gibbs energies of formation, listed in Tables 1 to 8, were obtained from two principal sources [Robie et al., 1979, and Wagman et al., 1982]. Both sources refer to a standard state of $T = 298.15\text{K}$, $P = 10^5\text{Pa}$, and for aqueous species a hypothetical 1 molal (1 mol per kg H_2O) ideal solution. These two compilations were used because they are complementary to a degree, and because the few major discrepancies highlight some of the experimental uncertainties. Robie et al. include error estimates (2σ) and literature sources, which are not given by Wagman et al. Some additional data have been gleaned from compilations by Sadiq and Lindsay [1979] and Naumov et al. [1971], and from the primary literature. Little effort has been made to assess critically the data presented here, but important omissions, uncertainties and discrepancies are noted. The sequence of the elements in the following discussion parallels Section 3.

4.1 ALKALI METALS

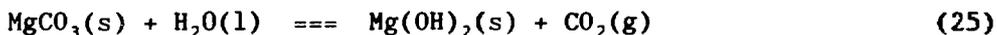
The high solubilities of alkali metal carbonates and bicarbonates are virtually common knowledge. The solubilities compiled by Whaley [1973] and Hart and Beumel [1973] suffice to rule these compounds out as ^{14}C waste forms.

4.2 ALKALINE EARTH ELEMENTS

There is generally good agreement between Robie et al. [1979] and Wagman et al. [1982] for species containing these elements (Tables 1 and 8). There is a major discrepancy of $17.4 \text{ kJ}\cdot\text{mol}^{-1}$, which corresponds to three orders of magnitude in the simple solubility product, for MgCO_3 . We prefer the more negative value given by Robie et al., because it is more consistent with the detailed discussion of magnesium carbonate phase relationships by Lippmann [1973]. The Gibbs energy data from Robie et al. yield the following equilibrium relationships:

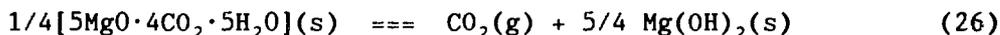


$$\Delta G_r = 46.8 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{24} = -8.2$$

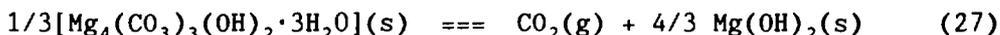


$$\Delta G_r = 38.7 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-1.8} \text{ Pa}$$

The apparent huge discrepancy between the Gibbs energies of hydromagnesite given by Robie et al. [1979] and Garrels et al. [1960] arises from the different stoichiometries that were assigned to this material: $5\text{MgO}\cdot 4\text{CO}_2\cdot 5\text{H}_2\text{O}$ and $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2\cdot 3\text{H}_2\text{O}$, respectively. These two sources are in fair agreement on the stability of hydromagnesite with respect to $\text{Mg}(\text{OH})_2$ (brucite):



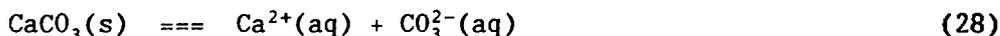
$$\Delta G_r = + 29.8 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-0.2} \text{ Pa}$$



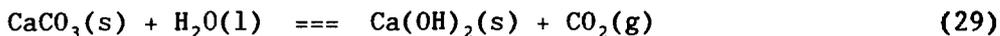
$$\Delta G_r = + 40.0 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-2.0} \text{ Pa}$$

The data given by Wagman et al. for an unnamed compound, $3\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ [$\equiv\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2\cdot 3\text{H}_2\text{O}$] yields $p(\text{CO}_2) = 10^{0.0}\text{Pa}$ for equilibrium (27). Calculations for equilibria of the same form as (26) and (27) indicate the following limits of stability of other magnesium carbonates with respect to brucite, $\text{Mg}(\text{OH})_2$: Nesquehonite, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$, $p(\text{CO}_2) = 10^{0.8}\text{Pa}$ [Wagman] or $10^{1.2}\text{Pa}$ [Robie]; Lansfordite, $\text{MgCO}_3\cdot 5\text{H}_2\text{O}$, $p(\text{CO}_2) = 10^{1.0}\text{Pa}$; Artinite, $\text{Mg}_2(\text{OH})_2\text{CO}_3\cdot 3\text{H}_2\text{O}$, $p(\text{CO}_2) = 10^{-0.7}\text{Pa}$. Thus, all these hydrated and basic magnesium carbonates have higher equilibrium partial pressures than magnesite (MgCO_3) with respect to brucite. This is consistent with Lippmann's [1973] conclusion that magnesite is the only stable solid carbonate in the system $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ near ambient temperature and pressure. Some additional, less common basic magnesium carbonates, including the minerals dypingite, giorgiosite and barringtonite, are discussed in a recent paper by Canterford et al. [1984].

There appears to be general agreement that calcite is the most stable form of CaCO_3 under ambient conditions, although its margin of stability over aragonite, vaterite and monohydrocalcite is small. Gibbs energy data yield the following equilibrium relationships:



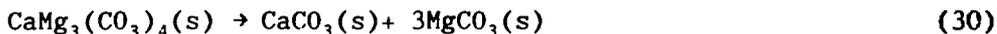
$$\Delta G_r = 47.4 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{28} = -8.3$$



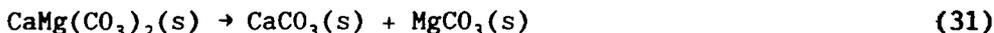
$$\Delta G_r = 73.1 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-7.8} \text{ Pa}$$

Thus, calcite and magnesite have almost identical solubilities, but calcite is much more stable than magnesite towards hydrolysis.

The differences in stability between the double carbonates, huntite ($\text{CaMg}_3(\text{CO}_3)_4$) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) and their simple carbonate components are small, so they offer no obvious advantages as waste forms:

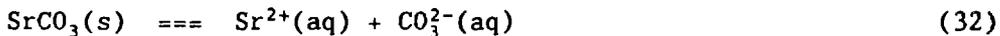


$$\Delta G_r = -13.9 \text{ kJ}\cdot\text{mol}^{-1} \text{ (huntite unstable)}$$

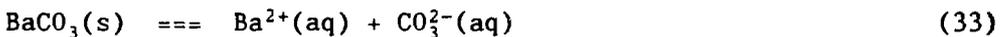


$$\Delta G_r = +3.4 \text{ kJ}\cdot\text{mol}^{-1} \text{ (dolomite stable)}$$

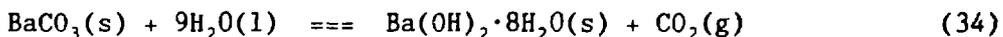
There is a little confusion in the thermodynamic literature on strontium and barium carbonates. The Gibbs energies listed by Wagman et al. [1982] yield the following equilibrium relationships:



$$\Delta G_r = 52.8 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{32} = -9.3$$

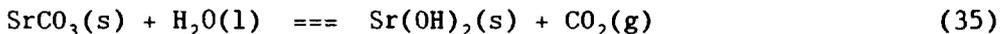


$$\Delta G_r = 49.0 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{33} = -8.6$$



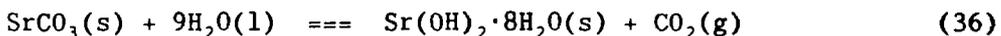
$$\Delta G_r = 78.9 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{34} = 10^{-8.8} \text{ Pa}$$

Neither Wagman et al. [1982] nor Robie et al. [1979] list any Gibbs energies for strontium hydroxides. Combining the value for $\text{Sr}(\text{OH})_2$ given by Chase et al. [1978] with other data from Wagman et al., we obtain:



$$\Delta G_r = 100.6 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-12.6} \text{ Pa}$$

Since $\text{Sr}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ is the stable form of strontium hydroxide in aqueous systems at 25°C, the equilibrium $p(\text{CO}_2)$ value for reaction (36) is expected to be slightly higher than for reaction (35):

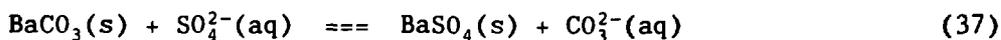


Robie et al. list somewhat less negative Gibbs energies of formation than Wagman et al. for both SrCO_3 and BaCO_3 , yielding $\log K_{32} = -8.8$ and $\log K_{33} = -7.6$. However, the value given by Wagman et al. for SrCO_3 is in better agreement with the solubility determined in a detailed study of strontianite dissolution ($\log K_{32} = -9.235$ at 25°C: Sonderegger et al. [1976]). Also, their value for BaCO_3 is more consistent with the solubility determination by Garrels et al. [1960].

Adami and Conway [1966] reported much lower Gibbs energies for SrCO_3 and BaCO_3 than those recommended by Wagman et al. However, these discrepancies arise from their choice of reference thermodynamic data for SrO and BaO , rather than any significant experimental disagreement on the behaviour of the carbonates.

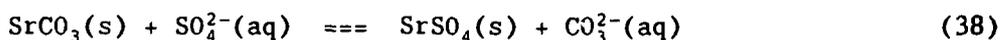
In conclusion, we favour the data listed by Wagman et al. for SrCO_3 and BaCO_3 , although the information available has not been exhaustively reviewed. These data indicate that SrCO_3 is the least soluble of the alkaline earth carbonates, but the differences between CaCO_3 , SrCO_3 and BaCO_3 are not large. All have favourably low susceptibility to hydrolysis (equations (29), (34) and (35)), with SrCO_3 again probably having the edge.

The following equilibrium relationships demonstrate that BaCO₃ is much more susceptible than either SrCO₃ or CaCO₃ to alteration by sulfate-containing groundwaters.



$$K_{37} = \{\text{CO}_3^{2-}\}/\{\text{SO}_4^{2-}\}, \text{ identical to } K_{11}.$$

$$\Delta G_r = -7.9 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{37} = 1.4$$



$$\Delta G_r = 15.8 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{38} = -2.8$$



$$\Delta G_r = 22.5 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{39} = -3.9$$

This is directly related to the much lower solubility of BaSO₄ (10^{-5.0} mol·dm⁻³) than either SrSO₄ (10^{-3.2} mol·dm⁻³) or CaSO₄·2H₂O (10^{-2.2} mol·dm⁻³).

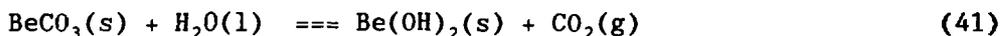
As noted above for calcium magnesium carbonates, the difference in stability between the two forms of BaCa(CO₃)₂ and their component carbonates are marginal:



$$\Delta G_r = 6.3 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Alstonite)}$$

$$5.4 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Barytocalcite)}.$$

Thermodynamic information on beryllium carbonates is limited to a Gibbs energy of formation of -948.1 kJ·mol⁻¹ for BeCO₃ [Naumov et al., 1971], whence:

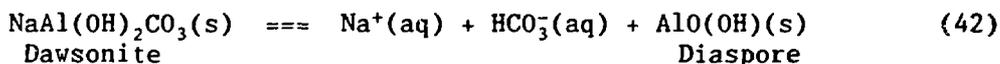


$$\Delta G_r = -26.7 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{+9.7} \text{ Pa}$$

This p(CO₂) value may be unrealistically high, but it indicates that BeCO₃ is unstable in aqueous systems.

4.3 OTHER MAIN-GROUP (p-BLOCK) ELEMENTS

Apart from the lead and bismuth systems, most of the comments on these elements were derived from general inorganic chemistry, rather than thermodynamic sources. The statement about the marginal stability of dawsonite is based on the following reaction:



$$\log K_{42} = \{\text{Na}^+\}\{\text{HCO}_3^-\}$$

$$\Delta G_r = 15.2 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{42} = -2.7$$

This indicates that dawsonite is stable, with respect to diaspore, only at high sodium and bicarbonate activities.

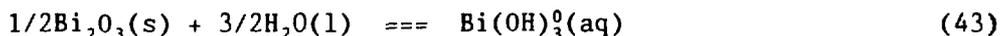
One apparent error in Wagman's compilation is the inclusion of data for solid Pb(OH)_2 , which indicate that it is stable with respect to $\text{PbO} + \text{H}_2\text{O}$, by a margin of $26 \text{ kJ}\cdot\text{mol}^{-1}$. Newkirk and Hughes [1970] concluded that reports of solid Pb(OH)_2 were erroneous, and most could be attributed to misidentification of basic lead nitrates. There appears to be cause for similar skepticism about the reports of BiOOH and Bi(OH)_3 . Wagman et al. give a Gibbs formation energy for $\text{PbO}\cdot\frac{1}{3}\text{H}_2\text{O}$ (sometimes referred to as $3\text{PbO}\cdot\text{H}_2\text{O}$ or $\text{Pb}_6\text{O}_4(\text{OH})_4$) that indicates it is marginally unstable with respect to $\text{PbO} + \frac{1}{3}\text{H}_2\text{O}$. This is consistent with its preparation from slightly supersaturated solutions of PbO [Todd and Parry, 1964], although the solubility data reported by Randall and Spencer [1928] indicated that it may be marginally stable.

Data for the lead carbonate system are taken from the paper by Taylor and Lopata [1984], which describes experimental measurements of equilibrium relationships between solids in the system $\text{PbO}-\text{CO}_2-\text{H}_2\text{O}$, and includes selected thermodynamic data for the numerous dissolved lead species. These data were derived mainly from the compilation by Sadiq and Lindsay [1979]. There are some discrepancies between this and the listing by Wagman et al. [1982], the most important being in the data for PbOH^+ ; the two sets of data are listed in Table 5. Figure 4 is adapted from Figures 3 and 4 of Taylor and Lopata [1984].

Alteration to sulfur-containing minerals must also be taken into account in assessing hydrocerussite as a ^{14}C waste-form. Calculations reported by Garrels and Christ [1965, pp. 233-238] indicate that alteration to anglesite (PbSO_4) or galena (PbS) is only likely in acidic or strongly reducing waters, respectively. However, phase relationships among basic lead sulfates are complex. [Abdul-Samad et al., 1982a and 1982b], and these may become important in slightly alkaline solutions. Several basic lead carbonate sulfate minerals are also known [Russell et al., 1984]. Alteration to other phases, such as phosgenite ($\text{Pb}_2(\text{CO}_3)\text{Cl}_2$) may occur in concentrated brines.

The only thermodynamic data for bismuth carbonates appear to be the Gibbs formation energies for $(\text{BiO})_2\text{CO}_3$ and $(\text{BiO})_4(\text{OH})_2\text{CO}_3$ reported by Taylor et al. [1984]. The former compound has been well characterized both as natural and synthetic material, but the latter had not been identified previously. There is no information on aqueous bismuth carbonate complexes.

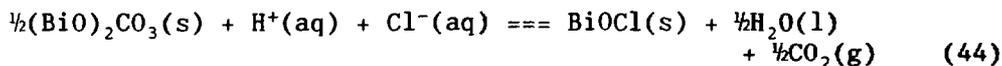
Several hydrolysed and polymeric aqueous bismuth species have been investigated by Olin and co-workers, as summarized by Baes and Mesmer [1976]. This work forms the basis for the Gibbs energy data listed by Wagman et al. [1982] and reproduced in Table 6. This compilation does not include the neutral species, $\text{Bi}(\text{OH})_3^0$. Baes and Mesmer, citing Bidleman [1971], indicate that this species controls the solubility of Bi_2O_3 at $10^{-5.4 \pm 0.1} \text{ mol} \cdot \text{dm}^{-3} \text{ Bi}$, in accordance with equation (43), over the pH range 7 to 13:



$$\log K_{43} = -5.4 \pm 0.1$$

From this, we estimate that $\Delta_f G^\circ = -571.6 \pm 2.2 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Bi}(\text{OH})_3^0$. This forms the basis for the calculation of K_{19} in the main text, and hence the predicted behaviour displayed in Figure 5. (Note that the error in K_{19} in the text is derived from errors in equilibrium constants, rather than in Gibbs energies; this gives a smaller error limit, because some common errors in the Gibbs energy calculation cancel out).

Our knowledge of bismuth sulfates is very limited, but the system is known to be complex. Unpublished work by Taylor and Lopata has shown that basic bismuth sulfates are more susceptible than the carbonates to hydrolysis to Bi_2O_3 . It seems likely that, as with the lead system, alteration of $(\text{BiO})_2\text{CO}_3$ to solid sulfates would only occur in acidic solutions. Conversion to Bi_2S_3 is only possible under strongly reducing conditions. Recent, unpublished work by Taylor and Lopata on stability relationships in the system $\text{Bi}_2\text{O}_3\text{-BiCl}_3\text{-H}_2\text{O-[pH]}$ indicates that $(\text{BiO})_2\text{CO}_3$ may be altered to BiOCl or other basic bismuth chlorides in acidic brines. This is consistent with the published Gibbs energy of formation of BiOCl (Table 8), which yields the following equilibrium relationship:



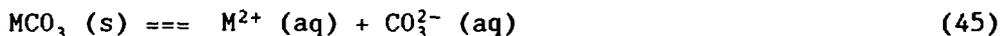
$$K_{44} = p(\text{CO}_2)^{1/2} / \{\text{H}^+\} \{\text{Cl}^-\} = 10^{8.5 \pm 0.6} \text{ Pa}^{1/2} \cdot \text{mol}^{-2} \cdot \text{dm}^6$$

From this expression, it is possible to determine whether $(\text{BiO})_2\text{CO}_3$ can be altered to BiOCl by a particular groundwater. Alteration to other basic chlorides may be possible at somewhat lower chloride activities, at given pH and $p(\text{CO}_2)$.

4.4 FIRST-ROW TRANSITION METALS

Gibbs energies of formation of some carbonates and relevant oxides and hydroxides of these elements are shown in Table 3. There are no major discrepancies between values recommended by Robie et al. [1979] and Wagman et al. [1982], but several species are only listed by one of these sources. In the following calculations, the Wagman data are used where possible, with Robie et al. as an alternate source. Some additional data were gleaned from other sources for some of the cobalt, copper and zinc compounds.

The data in Tables 3 and 8 allow us to calculate the equilibrium constants for the simple dissolution and decomposition reactions, (45) and (46), in the same way as for the alkaline earth carbonates (Section 5.2):



$$K_{45} = \{\text{M}^{2+}\} \{\text{CO}_3^{2-}\}$$

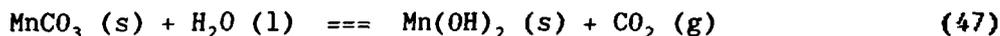


$$K_{46} = p(\text{CO}_2)$$

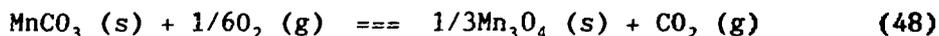
Values of $\log K_{45}$ and $\log K_{46}$ for $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn are given in Table 9.

The $\log K_{45}$ values, with the exception of NiCO_3 , lie between -9.6 and -10.6 , indicating that these carbonates are one to two orders of magnitude less soluble than the alkaline earth carbonates. However, with the exception of MnCO_3 , the decomposition pressures (K_{46}) are all very high. The anomalously high value of K_{45} for NiCO_3 suggests that the reported value of $\Delta_f G^\circ$ may be 15 to $20 \text{ kJ}\cdot\text{mol}^{-1}$ too high for this compound. However, even if this is so, the decomposition partial pressure would be about 10 Pa , which is still too high for our purposes. The data for CuCO_3 may also be questioned. The Gibbs energy given by Sadiq and Lindsay [1979] probably originates from Kelley and Anderson [1935], but Massey [1973] pointed out that "the pure carbonate has not been isolated". Since then, however, authentic CuCO_3 has been prepared at high pressures by Seidel et al. [1974]. Although the stated Gibbs formation energy of CuCO_3 is thus in doubt, there is little question that its decomposition pressure is high. Thus, MnCO_3 is the only one of these compounds that merits consideration as a carbon-14 waste form.

Since manganese occurs in several oxidation states, the partial pressure of oxygen must be taken into account in determining the equilibrium behaviour of MnCO_3 . Also, $\text{Mn}(\text{OH})_2$ is more stable than MnO in ambient aqueous systems. Therefore, the evolution of CO_2 from MnCO_3 is controlled by equilibria (47) to (50), which form the basis for Figure 7.

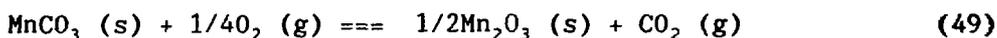


$$\Delta G_r = 44.4 \text{ kJ}\cdot\text{mol}^{-1}; p(\text{CO}_2) = 10^{-2.8} \text{ Pa}$$



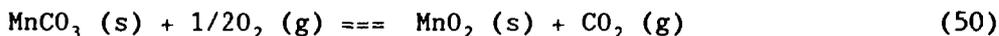
$$K_{48} = p(\text{CO}_2)/p(\text{O}_2)^{1/6}$$

$$\Delta G_r = -5.4 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{48} = 5.1 \text{ (pressures in Pa)}$$



$$K_{49} = p(\text{CO}_2)/p(\text{O}_2)^{1/4}$$

$$\Delta G_r = -18.3 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{49} = 7.0 \text{ (pressures in Pa)}$$



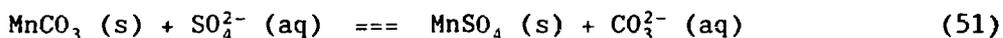
$$K_{50} = p(\text{CO}_2)/p(\text{O}_2)^{1/2} \neq$$

$$\Delta G_r = -42.8 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{50} = 10.0 \text{ (pressures in Pa)}$$

The equilibrium $p(\text{CO}_2)$ associated with $(\text{Mn}(\text{OH})_2 + \text{MnCO}_3)$ is substantially higher than with $(\text{MnO} + \text{MnCO}_3)$, but not high enough to rule out MnCO_3 altogether. Some caution is needed here, since Garrels et al. [1960] reported that the Gibbs energy of formation of synthetic precipitated MnCO_3 is about $4.2 \text{ kJ}\cdot\text{mol}^{-1}$ higher (i.e. less negative) than that of natural MnCO_3 (rhodochrosite). The corresponding difference in solubility products is almost an order of magnitude, the synthetic precipitate being more soluble. Also, the reported Gibbs energy of $\text{Mn}(\text{OH})_2$ refers to precipitated material, and may be correspondingly higher than the value for well-crystallized material. The $p(\text{CO}_2)$ associated with an assemblage of a fine-grained synthetic MnCO_3 and a well crystallized $\text{Mn}(\text{OH})_2$ alteration product could thus be as high as 10^{-1}Pa . This matter would have to be resolved before MnCO_3 could be recommended as a waste form for carbon-14.

Equilibria (48) to (50) show that the decomposition $p(\text{CO}_2)$ value of MnCO_3 increases with increasing $p(\text{O}_2)$ above 10^{-47} Pa ; this is depicted in Figure 7. Clearly, the disposal environment for $\text{Mn}^{14}\text{CO}_3$ would have to be reducing. A situation in which redox chemistry is controlled by the magnetite/hematite buffer would seem to be appropriate. The effective $p(\text{O}_2)$ of this buffer is 10^{-66} Pa at 25°C .

Alteration to MnSO_4 , according to equilibrium (51), is not a problem:



$$K_{51} = \{\text{CO}_3^{2-}\}/\{\text{SO}_4^{2-}\}$$

$$\Delta G_r = 76.1 \text{ kJ}\cdot\text{mol}^{-1}; \log K_{51} = -13.3$$

Hydrated MnSO_4 species are somewhat less soluble than the anhydrous salt at 25°C , but not sufficiently so to alter this conclusion [Kemmitt, 1973, and references therein].

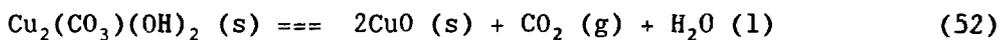
Gibbs energy data for dissolved manganese species, which form the basis for the calculated solubilities shown in Figure 6, are listed in Table 7. These are derived from equilibrium constants summarized by Baes

[‡] Gibbs energies refer to a standard pressure of 1 bar (10^5 Pa), but equilibrium constants refer to pressures in Pa, for consistency with the rest of this report.

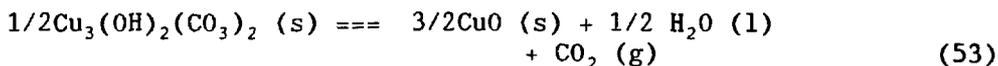
and Mesmer [1976], based on the Gibbs energy for Mn^{2+} given by Wagman et al. [1982]. Baes and Mesmer do not express full confidence in these equilibrium constants, so the information in Table 7 and Figure 6 should be regarded as preliminary. However, these data do indicate a substantial improvement in solubility over $CaCO_3$ in near-neutral solutions, although this is offset by lower stability in alkaline solutions. Note that the uncertainties in the data for $Mn(OH)_2$ and $MnCO_3$, discussed above, mean that the boundary between these phases in Figure 6 could be shifted to lower pH for either poorly crystallized $MnCO_3$ or well crystallized $Mn(OH)_2$.

The following statement on the properties of $MnCO_3$, by Kemmitt [1973], supports our conclusion that it has some merit as a possible waste form for ^{14}C : "The stability of manganese (II) carbonate is largely due to its insolubility... and the solid is only slightly hydrolysed even in boiling water. The pure salt is pink and slowly darkens in air due to air oxidation. The carbonate decomposes on heating to give oxides of manganese, the oxidation states of these oxides depending on whether the decomposition is performed in the absence or presence of oxygen."

There is little thermodynamic information on basic carbonates of the transition elements. The only well characterized compounds of this type appear to be malachite ($Cu_2(CO_3)(OH)_2$), azurite ($Cu_3(OH)_2(CO_3)_2$) and hydrozincite ($Zn_5(OH)_6(CO_3)_2$). Data given by Wagman et al. for the copper compounds yield the following relationships:



$$\Delta G_r = 2.7 \text{ kJ}\cdot\text{mol}^{-1}; p(CO_2) = 10^{4.5}\text{Pa}$$

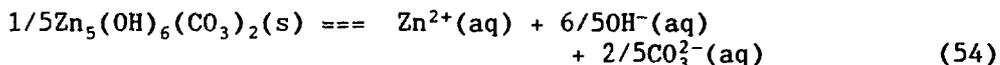


$$\Delta G_r = -49.8 \text{ kJ}\cdot\text{mol}^{-1}; p(CO_2) = 10^{13.7}\text{Pa}$$

These very high $p(CO_2)$ values indicate that the basic copper carbonates are unstable under ambient conditions. Garrels [1957] has suggested, however, that malachite is marginally stable ($p(CO_2) \approx 10^{1.3}\text{Pa}$), based on observations of malachite intergrown with tenorite in weathered copper deposits. Wagman's data for azurite are also at odds with other sources [Naumov et al., 1971; Sadiq and Lindsay, 1979], which indicate a much lower Gibbs energy of formation (Table 3), and a $p(CO_2)$ value of about 10^4Pa for equilibrium (53). This may be a little high, considering the widespread natural occurrence of azurite, but it is known to be unstable with respect to malachite in moist air. Vink [1986] has recently discussed the delicate balance in stability between malachite and azurite near ambient conditions, but did not present any new experimental information. More detailed investigations of basic copper salts, including these two carbonates, have been reported by Woods and Garrels [1986a, 1986b]. The data they recommend indicate that malachite is stable between $10^{2.5}$ and $10^{4.3}$ Pa, in the presence of liquid water. Outside these limits, it is unstable with respect to CuO (eq. (52)) and azurite, respectively.

Although there has thus been some debate about the exact stabilities of these basic carbonates, there is little question that they are too unstable to be considered as ^{14}C waste-forms.

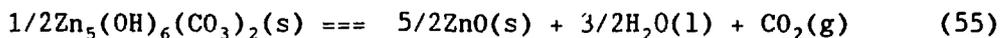
Alwan and Williams [1979] recently investigated the stability of hydrozincite, $Zn_5(OH)_6(CO_3)_2$. They analysed natural waters responsible for the formation of solid hydrozincite, and deduced the following relationships, where K_{53} corresponds to their K_{sp} .



$$K_{54} = \{Zn^{2+}\} \{OH^-\}^{1.2} \{CO_3^{2-}\}^{0.4}$$

$$\log K_{54} = -14.9 \pm 0.1,$$

whence:



$$p(CO_2) = 10^{-1.0} Pa$$

Hydrozincite is thus somewhat more stable than the basic copper carbonates, but not sufficiently so to be considered as a ^{14}C waste-form.

4.5 THE REMAINING ELEMENTS

Most of the discussion of these elements in Section 3.5 and 3.6 is based on general chemistry, rather than detailed consideration of solubility and stability. There is no need to elaborate further on the few thermodynamic statements in those sections. Relevant thermodynamic data are given in Tables 3 and 4.

5. CONCLUSIONS

Calcium and barium carbonates, either alone or incorporated in a concrete, are presently favoured by others as waste forms for immobilization and disposal of ^{14}C [Scheele and Burger, 1982]. Given the high solubility of these carbonates in non-alkaline solutions, care is needed to select an appropriate environment for their disposal. In this review, we have identified three compounds that warrant consideration as alternative waste forms; all of these offer improved solubility characteristics relative to $CaCO_3$ and $BaCO_3$ in near-neutral solutions. These compounds are (in order of increasing overall solubility) bismutite ($(BiO)_2CO_3$), hydrocerussite ($Pb_3(OH)_2(CO_3)_2$) and rhodochrosite ($MnCO_3$). No other simple or basic carbonates appear to offer any improvement over $CaCO_3$, although the lanthanide carbonate systems are too poorly understood to rule them out completely. There is a possibility that some more complex solids may offer improved properties, one such being La-bastnaesite, $LaFCO_3$.

Bismuth, lead, manganese and lanthanum are all much less abundant, and correspondingly more expensive, than calcium. However, the quantities required for ^{14}C disposal are sufficiently low that resource supply is unlikely to constrain the selection of a waste form from this short list, unless there is substantial isotopic dilution with ^{12}C . As well as having the lowest solubility over a wide range of pH, bismutite has the added advantage that bismuth has low toxicity.

ACKNOWLEDGEMENTS

I am grateful to V.J. Lopata for his help in computing the solubility behaviour depicted in Figures 4, 5, and 6, and to J. Paquette, R. Lemire and E.R. Vance for helpful comments and discussions.

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TABLE 1

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$,
FOR ALKALINE EARTH OXIDES, HYDROXIDES AND CARBONATES.

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	Wagman et al. [1982]	Robie et al. [1979]	Other [ref]
BeO (Bromellite)	-580.3	-580.1 ± 2.5	
β -Be(OH) ₂	-817.5	--	
BeCO ₃	ΔH only	--	-948.1[a]
MgO (Periclase)	-569.4	-569.2 ± 0.3	
Mg(OH) ₂ (Brucite)	-833.5	-833.5 ± 0.4	
MgCO ₃ (Magnesite)	-1012.1	-1029.5 ± 1.4	
MgCO ₃ ·3H ₂ O (Nesquehonite)	-1726.1	-1723.7 ± 0.5	
MgCO ₃ ·5H ₂ O (Lansfordite)	-2199.2	---	-2200.2[a]
5MgO·4CO ₂ ·5H ₂ O (Hydromagnesite)	--	-5864.2 ± 1.1 -4637.1 [Mg ₄ (CO ₃) ₃ (OH) ₂ ·3H ₂ O, b]	
Mg ₂ (OH) ₂ CO ₃ ·3H ₂ O (Artinite)	--	-2568.3 ± 0.8	

...continued

TABLE 1 (continued)

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	Wagman et al. [1982]	Robie et al. [1979]	Other [ref]
3MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O	-4603.3	--	-4637.1 [b]
CaO	-604.0	-603.5 ± 0.9	
Ca(OH) ₂ (Portlandite)	-898.5	-898.4 ± 1.3	
CaCO ₃ (Calcite)	-1128.8	-1128.8 ± 1.4	
CaCO ₃ (Aragonite)	-1127.8	-1127.8 ± 1.5	
CaCO ₃ (Vaterite)	--	-1125.5 ± 1.5	
CaCO ₃ ·H ₂ O (Monohydrocalcite)	--	-1361.6 ± 1.1	
CaMg(CO ₃) ₂ (Dolomite)	-2163.4	-2161.7 ± 1.7	
CaMg ₃ (CO ₃) ₄ (Huntite)	--	-4203.4 ± 1.6	
SrO	-561.9	-560.4 ± 0.9	
Sr(OH) ₂	ΔH only	--	-882.2 [c]

...continued

TABLE 1 (concluded)

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	Wagman et al. [1982]	Robie et al. [1979]	Other [ref]
Sr(OH) ₂ ·8H ₂ O	ΔH only	--	
SrCO ₃ (Strontianite)	-1140.1	-1137.6 ± 1.5	
BaO	-525.1	-520.4 ± 2.1	
Ba(OH) ₂	ΔH only	--	
Ba(OH) ₂ ·8H ₂ O	-2792.8	--	
BaCO ₃ (Witherite)	-1137.6	-1132.2 ± 2.2	
BaCa(CO ₃) ₂ (Alstonite)	-2272.7	--	
BaCa(CO ₃) ₂ (Barytocalcite)	-2271.8	--	

REFERENCES [for Table 1]

- a. Naumov et al. [1971]
- b. Garrels et al. [1960]
- c. Chase et al. [1978].

TABLE 2

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND CARBONATES OF p-BLOCK ELEMENTS, EXCLUDING ALKALI METALS AND ALKALINE EARTHS

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	<u>Wagman et al. [1982]</u>	<u>Robie et al. [1979]</u>	<u>Other [ref]</u>
Al ₂ O ₃ (Corundum)	-1582.3	-1582.2 ± 1.3	
AlO(OH) (Boehmite)	-915.9	-918.4 ± 2.1	
AlO(OH) (Diaspore)	-920.9	-922.0 ± 5.0	
Al(OH) ₃ (Gibbsite)	-1155.1	-1154.9 ± 1.2	
NaAlCO ₃ (OH) ₂ (Dawsonite)	---	-1786.0 ± 3.0	
TlOH		-195.8	--
Tl ₂ CO ₃	-614.6	--	
PbO (Litharge [red])		-188.93	-189.2 ± 0.9
PbO.1/3H ₂ O	-266.5	--	
Pb(OH) ₂	-452.2	--	
Pb ₁₀ O(OH) ₆ (CO ₃) ₆ (Plumbonacrite)	---	--	-5310 ± 31 [a]

...continued

TABLE 2 (concluded)

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND CARBONATES OF p-BLOCK ELEMENTS, EXCLUDING ALKALI METALS AND ALKALINE EARTHS

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	<u>Wagman et al. [1982]</u>	<u>Robie et al. [1979]</u>	<u>Other [ref]</u>
Pb ₃ (OH) ₂ (CO ₃) ₂ (Hydrocerussite)	---	--	-1705 ± 11 [a]; -1711.6[b]
PbCO ₃ (Cerussite)	-625.5	-625.3 ± 1.5	-628.0 ± 3.9[a]; -629.7[b]
α-Bi ₂ O ₃ (Bismite)	-493.7	-493.5 ± 1.5	
BiOOH	-368.1	--	
Bi(OH) ₃	ΔH Only	--	
(BiO) ₄ (OH) ₂ CO ₃	---	--	-1678 ± 9[c]
(BiO) ₂ CO ₃	---	-	-945 ± 7[c]

REFERENCES (For Table 2)

- a. Taylor and Lopata [1984].
- b. Sadiq and Lindsay [1979].
- c. Taylor, Sunder and Lopata [1984].

TABLE 3

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND
CARBONATES OF d-BLOCK TRANSITION ELEMENTS

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	<u>Wagman et al. [1982]</u>	<u>Robie et al. [1979]</u>	<u>Other [ref]</u>
MnO (Manganosite)	-362.9	-362.9 ± 0.5	
Mn ₃ O ₄ (Hausmannite)	-1283.2	-1282.8 ± 2.1	
Mn ₂ O ₃ (Bixbyite)	-881.1	-881.1 ± 2.2	
MnO ₂ (Pyrolusite)	-465.1	-465.1 ± 0.9	
Mn(OH) ₂ (pptd)	-615.0	--	-615.6[a]
MnCO ₃ (Rhodochrosite)	-816.7	-816.0 ± 1.4	
FeO	ΔH Only	-251.2 ± 2.2	
Fe ₃ O ₄ (Magnetite)	-1015.4	-1012.6 ± 2.1	
Fe ₂ O ₃ (Hematite)	-742.2	-742.7 ± 1.3	
FeO(OH) (Goethite)	ΔH Only	-488.6 ± 0.8	
FeCO ₃ (Siderite)	-666.7	-666.7 ± 2.1	
CoO	-214.2	-214.2 ± 1.3	
Co(OH) ₂ (aged)	-458.1	--	

...continued

TABLE 3 (continued)

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND
CARBONATES OF d-BLOCK TRANSITION ELEMENTS

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	Wagman et al. [1982]	Robie et al. [1979]	Other [ref]
Co ₃ O ₄	-774	--	
CoCO ₃ (Sphaerocobaltite)	ΔH Only	--	-640.2[b] -649.4[c]
NiO (Bunsenite)	-211.7	-211.6 ± 0.5	
Ni(OH) ₂	-447.2	--	
NiCO ₃	-612.5	--	-612.1[b]
Cu ₂ O (Cuprite)	-146.0	-146.0 ± 6.3	
CuO (Tenorite)	-129.7	-129.6 ± 1.3	
Cu(OH) ₂	ΔH Only	--	
Cu ₂ (CO ₃)(OH) ₂ (Malachite)	-893.6	ΔH Only	-901.3[b] -900.6[d] -905.0[e]
Cu ₃ (OH) ₂ (CO ₃) ₂ (Azurite)	-1315.5	ΔH Only	-1430.9[b] -1429.1[d] -1438.2[e]
CuCO ₃	---	--	-517.4[d]
ZnO (Zincite)	-318.3	-320.5 ± 0.3	
ϵ -Zn(OH) ₂	-555.1	--	

...continued

TABLE 3 (concluded)

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND
CARBONATES OF d-BLOCK TRANSITION ELEMENTS

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	<u>Wagman et al. [1982]</u>	<u>Robie et al. [1979]</u>	<u>Other [ref]</u>
Zn ₅ (OH) ₆ (CO ₃) ₂ (Hydrozincite)	---	--	-3161.6[f]
ZnCO ₃ (Smithsonite)	-731.5	-731.5 ± 3.0	
ZnCO ₃ ·H ₂ O	-970.6	--	
CdO (Monteponite)	-228.4	-228.5 ± 0.9	
Cd(OH) ₂ (pptd)	-473.6	--	
CdCO ₃ (Otavite)	-669.4	-669.4 ± 2.6	
Ag ₂ O	-11.2	--	
Ag ₂ CO ₃	-436.8	--	-436.9 ± 2.1[b]
HgO (Montroydite)	-58.5	-58.5 ± 0.1	
Hg ₂ CO ₃	-468.1	--	-454.0[d]
HgCO ₃	---	--	-492.1[d]

REFERENCES

- a. Derived from Baes and Mesmer [1976].
- b. Naumov et al. [1971].
- c. Garrels and Christ [1965].
- d. Sadiq and Lindsay [1979].
- e. Woods and Garrels [1986a].
- f. Derived from Alwan and Williams [1979].

TABLE 4

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR SOME OXIDES, HYDROXIDES AND
CARBONATES OF LANTHANUM, PRASEODYMIUM AND URANIUM

FORMULA AND (MINERAL NAME)	$\Delta_f G^\circ$, kJ·mol ⁻¹		
	<u>Wagman et al. [1982]</u>	<u>Robie et al. [1979]</u>	<u>Other [ref]</u>
La ₂ O ₃	-1705.8	-1706.0 ± 1.6	
La(OH) ₃	ΔH Only	--	
La ₂ (CO ₃) ₃	-3141.6	--	
γ-UO ₃	-1145.9	-1146.5 ± 1.0	-1146 ± 2[a]
β-UO ₂ (OH) ₂	-1394.8	--	-1394 ± 4[a]
UO ₃ ·2H ₂ O	-1630.8	--	-1632 ± 2[a]
UO ₂ CO ₃ (Rutherfordine)	-1562.6	--	-1561 ± 2 [a]
Pr ₂ O ₃	---	-1721.0 ± 6.7	
Pr(OH) ₃	-1284.8	--	
Pr ₂ (CO ₃) ₃	ΔH Only	--	

REFERENCE

a. Lemire and Tremaine [1980].

TABLE 5

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR LEAD SPECIES IN AQUEOUS SOLUTIONS

<u>SPECIES</u>	$\Delta_f G^\circ$, kJ·mol ⁻¹	
	<u>Taylor and Lopata[1984]</u>	<u>Wagman et al. [1982]</u>
Pb ²⁺	-24.7	-24.4
PbOH ⁺	-217.9	-226.3
Pb(OH) ₂ ⁰	-397.7	-400.8
Pb(OH) ₃ ⁻	-575.9	-575.6
Pb ₂ OH ³⁺	-250.0	--
Pb ₃ (OH) ₄ ²⁺	-886.4	-888.6
Pb ₄ (OH) ₄ ⁴⁺	-928.2	-936.3
Pb ₆ O(OH) ₆ ⁴⁺	-1559.6	-1563.1*
PbCO ₃ ⁰	-593.4	--
Pb(CO ₃) ₂ ²⁻	-1141.2	--

*Derived from value for "Pb₆(OH)₈⁴⁺", which is equivalent to Pb₆O(OH)₆⁴⁺ + H₂O; see Taylor and Lopata [1984].

TABLE 6

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR BISMUTH SPECIES IN AQUEOUS SOLUTIONS(from Wagman et al., [1982])

SPECIES	$\Delta_f G^\circ$, kJ·mol ⁻¹
Bi ³⁺	+82.8
BiO ⁺	-146.4
Bi ₆ O ₆ ⁶⁺	-928.0
BiOH ²⁺	-146.4
Bi ₆ O ₆ (OH) ₃ ³⁺	-1588.1
Bi ₆ (OH) ₁₂ ⁶⁺	-2350.7
Bi ₉ (OH) ₂₀ ⁷⁺	-3980.5
Bi ₉ (OH) ₂₁ ⁶⁺	-4199.3
Bi(OH) ₂₂ ⁵⁺	-4421.4
Bi(OH) ₃ ⁰	-571.6 (see text, p. 26)

TABLE 7

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR MANGANESE SPECIES IN AQUEOUS SOLUTION

SPECIES	$\Delta_f G^\circ$, kJ·mol ⁻¹	
	Derived From Baes and Mesmer [1976]	Wagman et al. [1982]
Mn ²⁺	--	-228.1
MnOH ⁺	-404.8	-405.0
Mn(OH) ₂ ⁰	-575.6	--
Mn(OH) ₃ ⁻	-740.9	-744.2
Mn(OH) ₄ ²⁻	-900.9	--
Mn ₂ OH ³⁺	-633.1	--
Mn ₂ (OH) ₃ ⁺	-1031.2	--
MnHCO ₃ ⁺	-832.0	-820

TABLE 8

GIBBS ENERGIES OF FORMATION, $\Delta_f G^\circ$, FOR ADDITIONAL SPECIES DISCUSSED IN THE TEXT

SPECIES	STATE	$\Delta_f G^\circ$, kJ·mol ⁻¹ *
H ₂ O	Liquid	-237.1 ± 0.1
CO ₂	Gas	-394.4 ± 0.2
"H ₂ CO ₃ "	Aqueous	-623.2 ± 0.1
OH ⁻	Aqueous	-157.3 ± 0.1
HCO ₃ ⁻	Aqueous	-586.9 ± 0.1
CO ₃ ²⁻	Aqueous	-527.9 ± 0.1
SO ₄ ²⁻	Aqueous	-744.6 ± 0.1
H ⁺	Aqueous	0
Na ⁺	Aqueous	-261.9 ± 0.1
Mg ²⁺	Aqueous	-454.8 ± 1.7
Ca ²⁺	Aqueous	-553.5 ± 1.2
Sr ²⁺	Aqueous	-559.4 ± 0.1
Ba ²⁺	Aqueous	-560.7 ± 0.1

...continued

TABLE 8 (concluded)

<u>SPECIES</u>	<u>STATE</u>	<u>$\Delta_f G^\circ$, kJ·mol⁻¹*</u>
Mn ²⁺	Aqueous	-228.0 ± 0.9
Fe ²⁺	Aqueous	-78.9 ± 1.0
Co ²⁺	Aqueous	-54.4 ± 0.5
Ni ²⁺	Aqueous	-45.6 ± 0.9
Cu ²⁺	Aqueous	+65.5 ± 0.1
Zn ²⁺	Aqueous	-147.3 ± 0.2
CaSO ₄ ·2H ₂ O	Solid (gypsum)	-1797.2 ± 4.6
SrSO ₄	Solid (celestite)	-1341.0 ± 4.0
BaSO ₄	Solid (barite)	-1362.2 ± 1.3
MnSO ₄	Solid	-957,3 ± 1.3
PbSO ₄	Solid (anglesite)	-813.0 ± 1.0
BiOCl	Solid (bismoclite)	-322.1 [Wagman et al., 1982]

* Data from Robie et al. [1979]. These agree within ± 0.1 kJ·mol⁻¹ with Wagman et al. [1982], except for Zn²⁺, for which Wagman et al. gives $\Delta_f G^\circ = 147.1$ kJ·mol⁻¹.

TABLE 9

EQUILIBRIUM RELATIONSHIPS FOR TRANSITION METAL CARBONATES, MCO_3 [‡]

M	log K_{44}	log (K_{45}, Pa)
Mn	-10.6	-5.4
Fe	-10.5	+1.3
Co	-10.1	-0.5
Ni	-6.8	+3.9
Cu	-9.6	+6.2
Zn	-9.9	+1.7

[‡] Based on Gibbs energy data from Wagman et al. [1982] (see Tables 3 and 8) except for $CoCO_3$ [Naumov et al., 1971] and $CuCO_3$ [Sadiq and Lindsay, 1979].

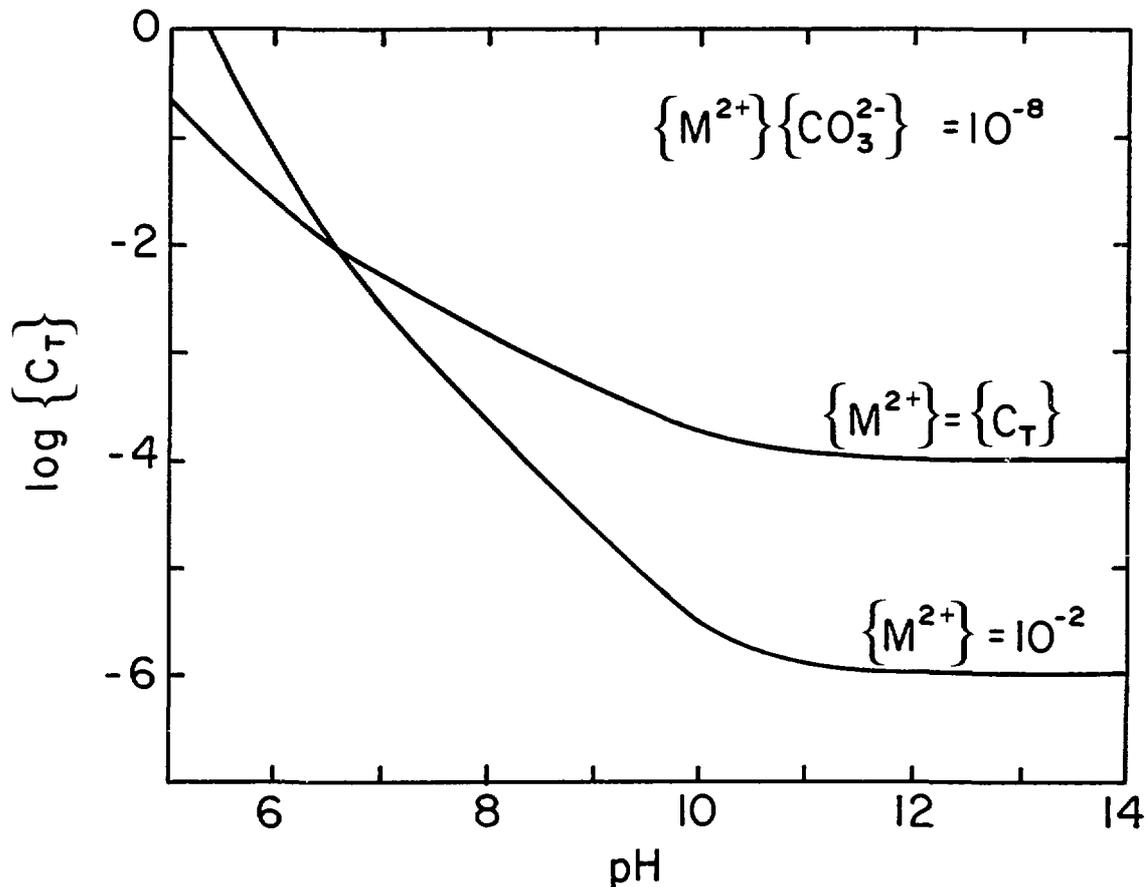


FIGURE 1.

Solubility, Expressed as Total Carbonate Activity $\{C_T\}$, of a Carbonate, MCO_3 , with a Solubility Product, K_{sp} , of $10^{-8} \text{ mol}^2 \cdot \text{dm}^{-6}$ (see equations 1 and 2). The cation, M^{2+} , does not hydrolyse or complex. The curve labelled " $\{M^{2+}\} = \{C_T\}$ " represents congruent dissolution, i.e. the solid is the sole source of dissolved metal and carbonate. (This curve is not corrected for ionic strength effects, which become significant at solubilities above about $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$. The other curve represents external control of the metal ion activity at $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$. Note the sharp increase in solubility at $\text{pH} < 11$ in both cases.

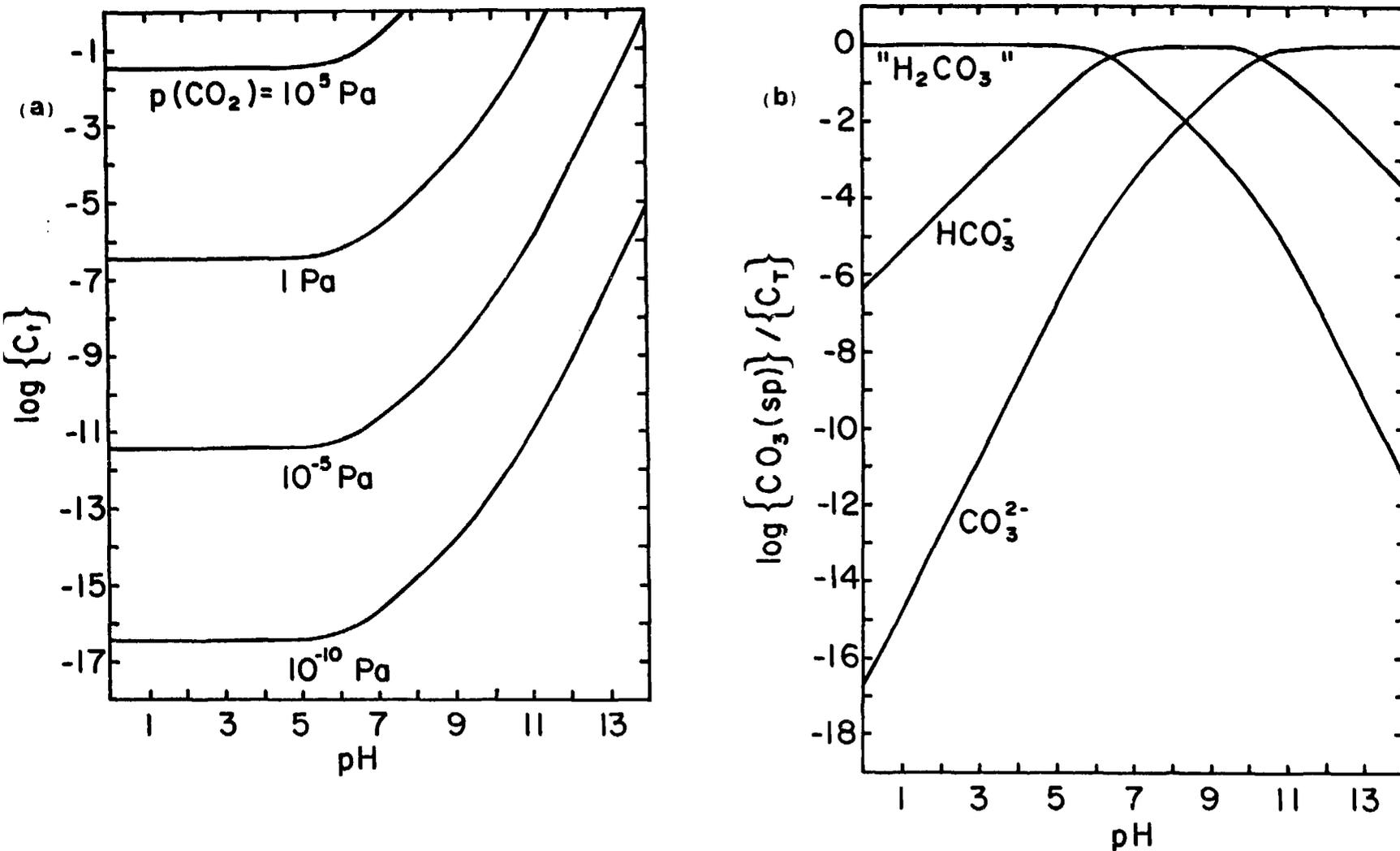


FIGURE 2.(a) Relationship between Total Carbonate Activity, $\{C_T\}$ and Carbon Dioxide Partial Pressure, $p(\text{CO}_2)$, as a Function of pH.

(b) Relative Activities of H_2CO_3 , HCO_3^- and CO_3^{2-} in Aqueous Solutions, as a Function of pH.

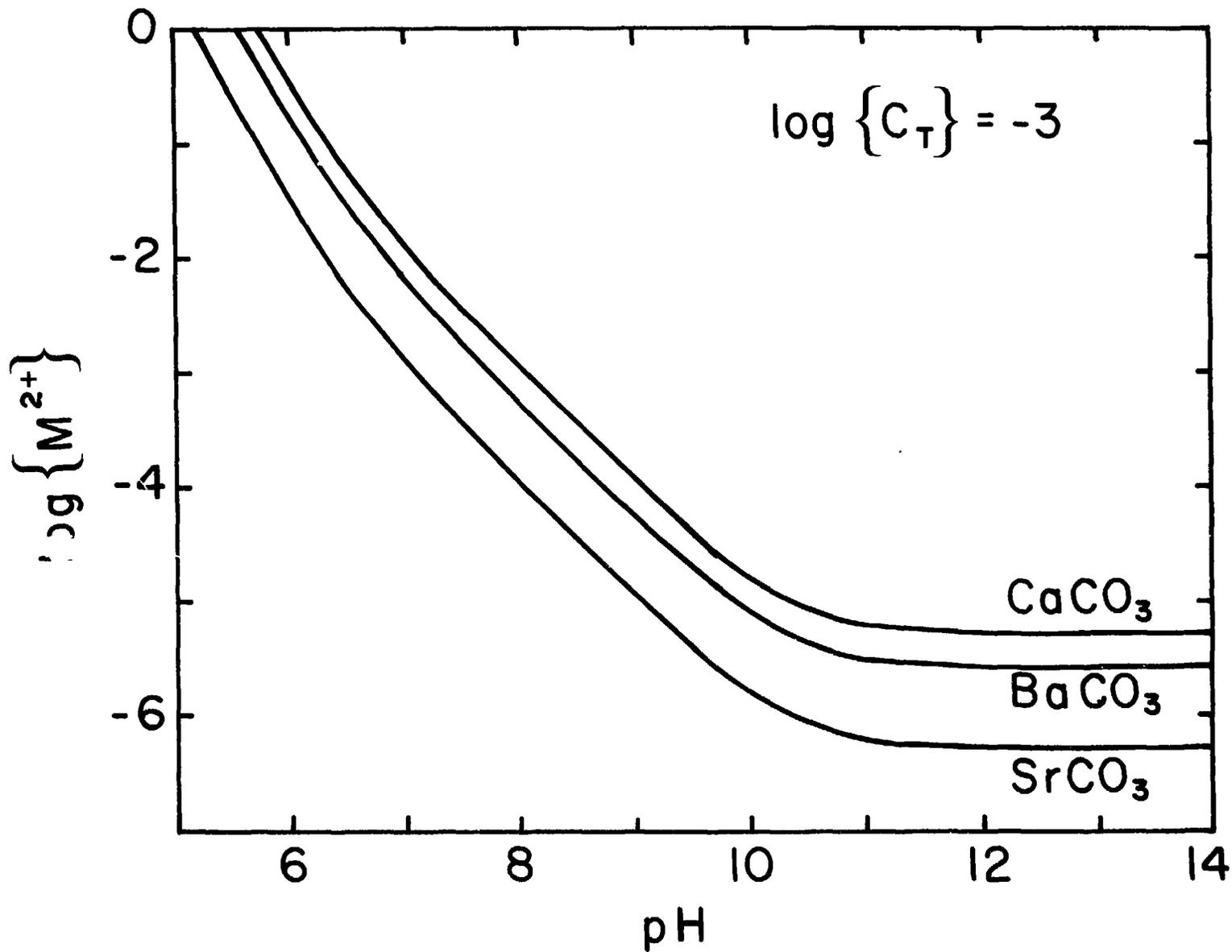


FIGURE 3. Calculated Equilibrium Activities of Ca^{2+} , Sr^{2+} and Ba^{2+} in Aqueous Solutions in Contact with $CaCO_3$, $SrCO_3$ and $BaCO_3$, at Constant Total Carbonate Activity of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$.

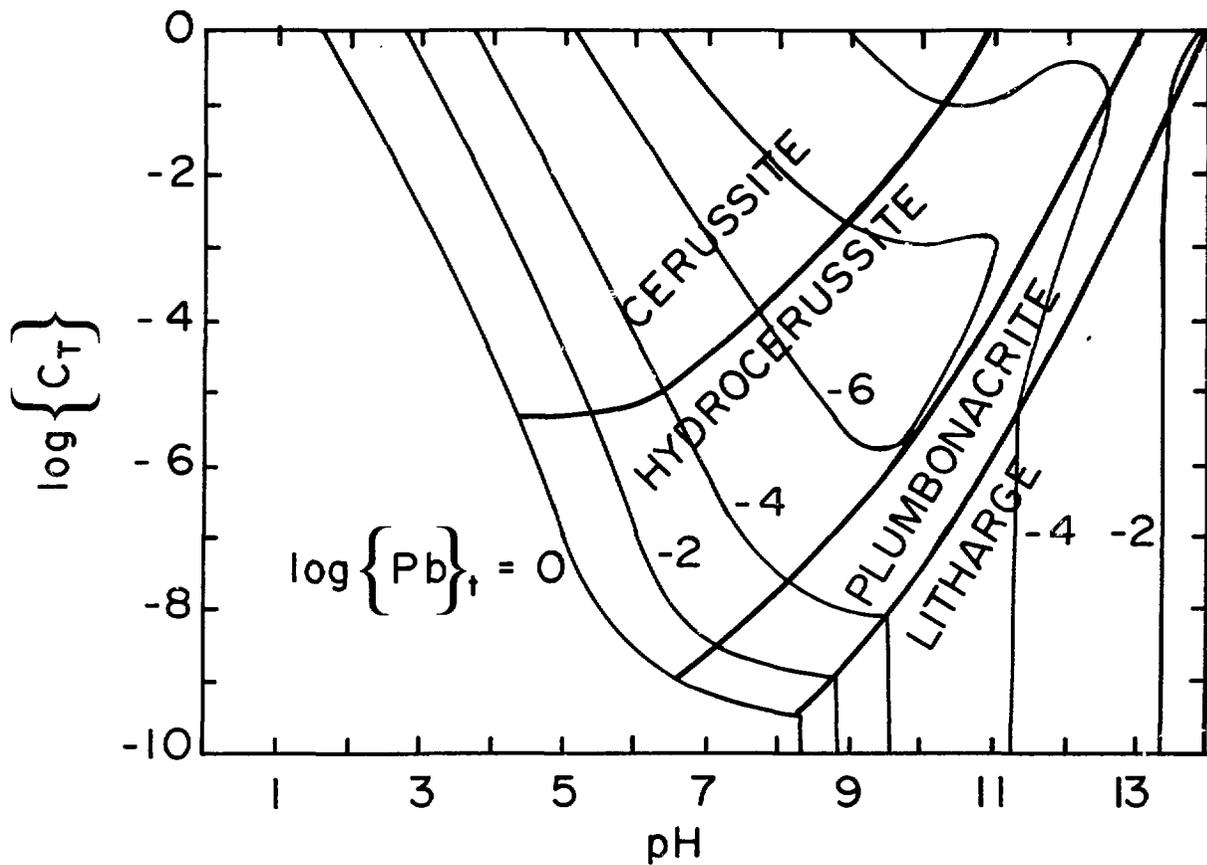


FIGURE 4. Calculated Solubility/Stability Relationships Between PbO (Litharge), $Pb_{10}O(OH)_6(CO_3)_6$ (Plumbonacrite), $Pb_3(OH)_2(CO_3)_2$ (Hydrocerussite) and $PbCO_3$ (Cerussite), Derived from Figure 4 and Table 3 of Taylor and Lopata (1984). Contours show total dissolved lead activity (including carbonate complexes and hydrolysed species) as a function of pH and $\{C_T\}$. Bold lines are solid stability boundaries.

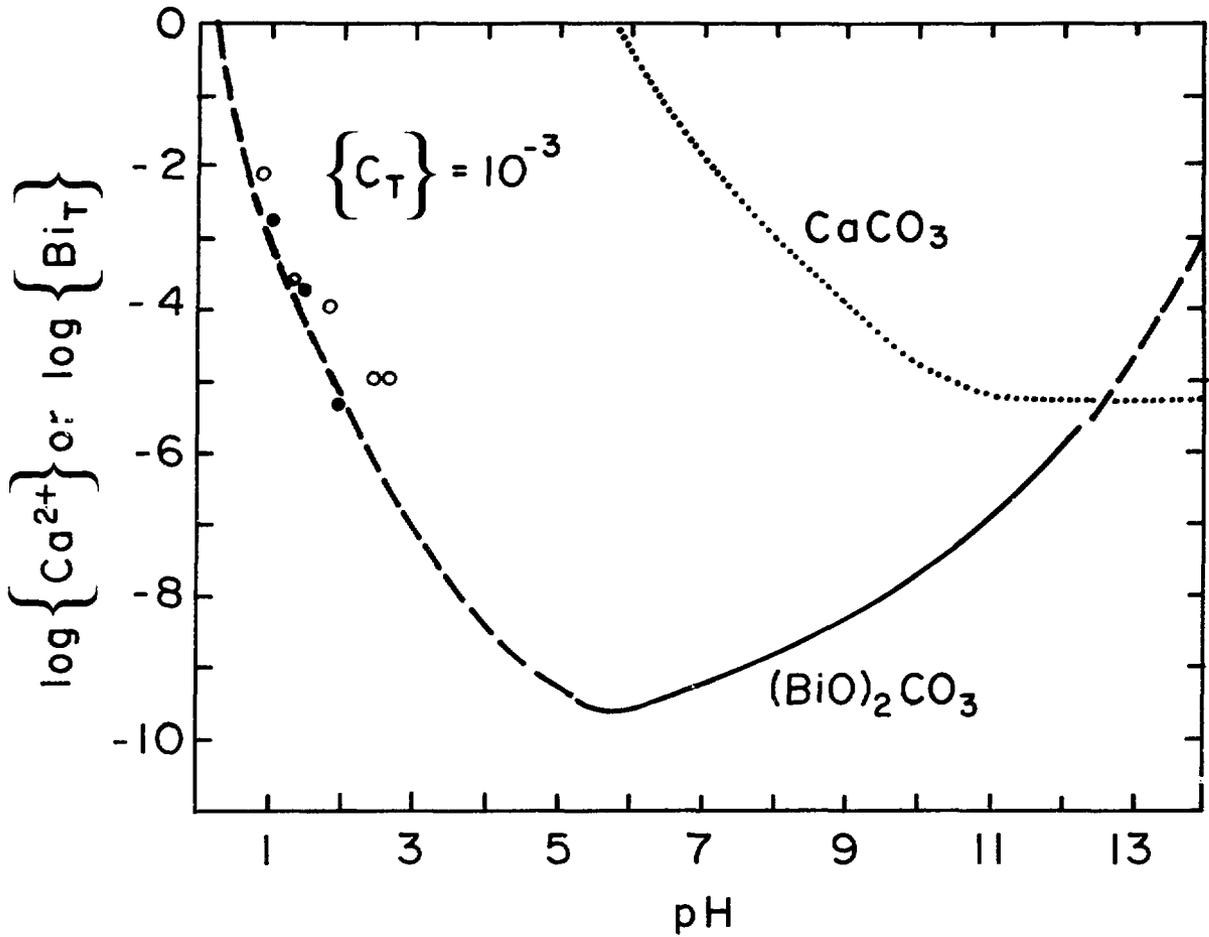


FIGURE 5. Calculated Dissolved Calcium and Total Dissolved Bismuth Activities in Equilibrium with $CaCO_3$ (Calcite) and $(BiO)_2CO_3$ (Bismutite), Respectively, at a Constant $\{C_T\}$ of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. The solid line represents control of dissolved bismuth by equation 19. Dashed lines represent areas where other bismuth species are important, and are estimated from information summarized by Baes and Mesmer (1976). Bismutite is unstable with respect to $(BiO)_4(OH)_2CO_3$ at $p(CO_2) < 10^{-4.4} \text{ Pa}$ ($pH < 12.3$ in this case) [Taylor et al., 1984]. Data points represent preliminary solubility measurements in CO_2 -saturated (\bullet) and air-saturated (\circ) solutions.

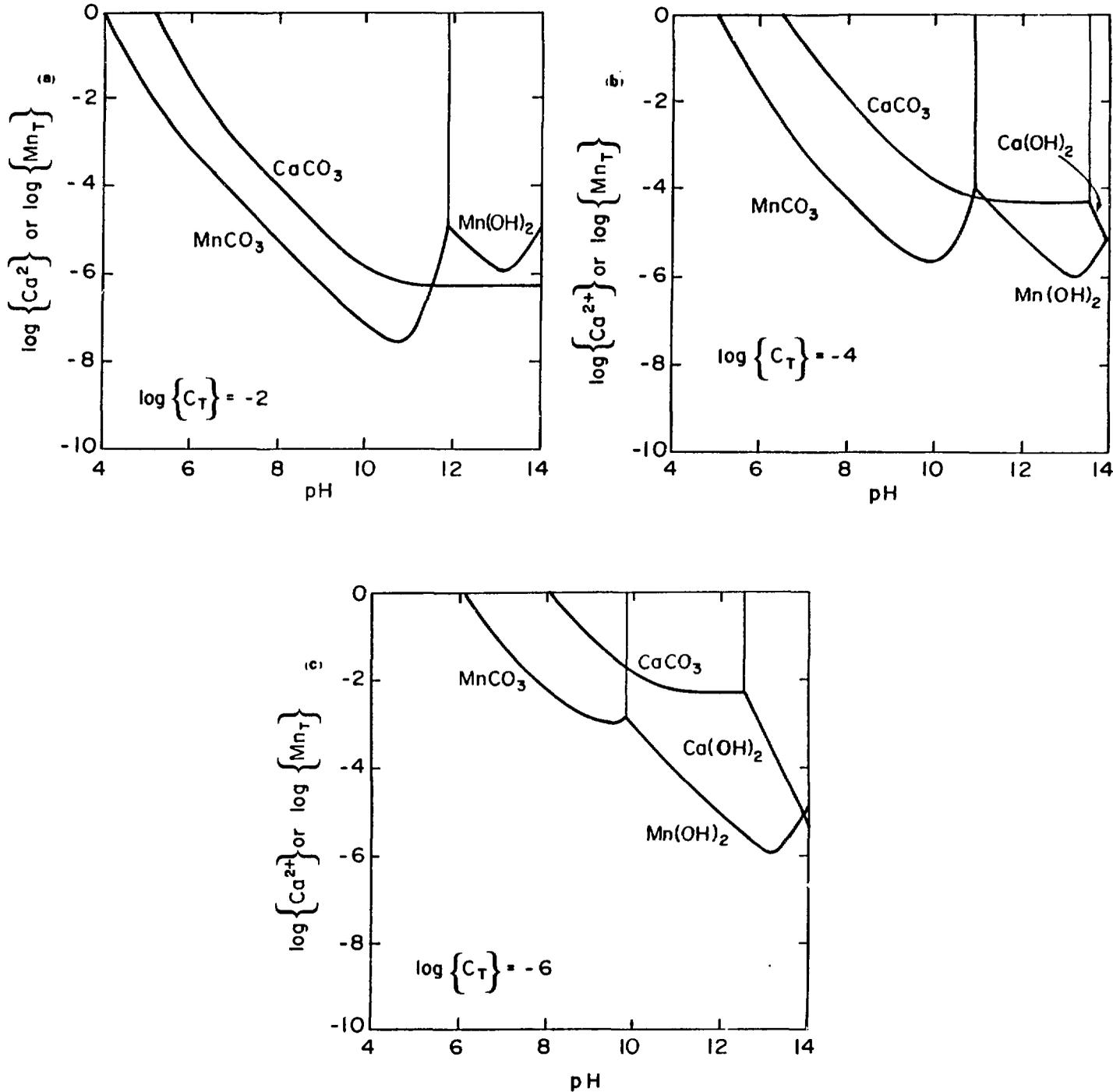


FIGURE 6. Calculated Total Manganese Activity and $\{Ca^{2+}\}$ for solutions in Equilibrium with $MnCO_3$ or $Mn(OH)_2$, and $CaCO_3$ or $Ca(OH)_2$, as a Function of pH, at Constant $\{C_T\}$ Values of (a) $10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, (b) $10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, and (c) $10^{-6} \text{ mol}\cdot\text{dm}^{-3}$. Note the lower solubility of $MnCO_3$ than $CaCO_3$ in near-neutral solutions, but remember the reservations expressed in the text about the manganese data-base. These figures refer to reducing conditions, under which Mn(II) is stable (see Figure 7).

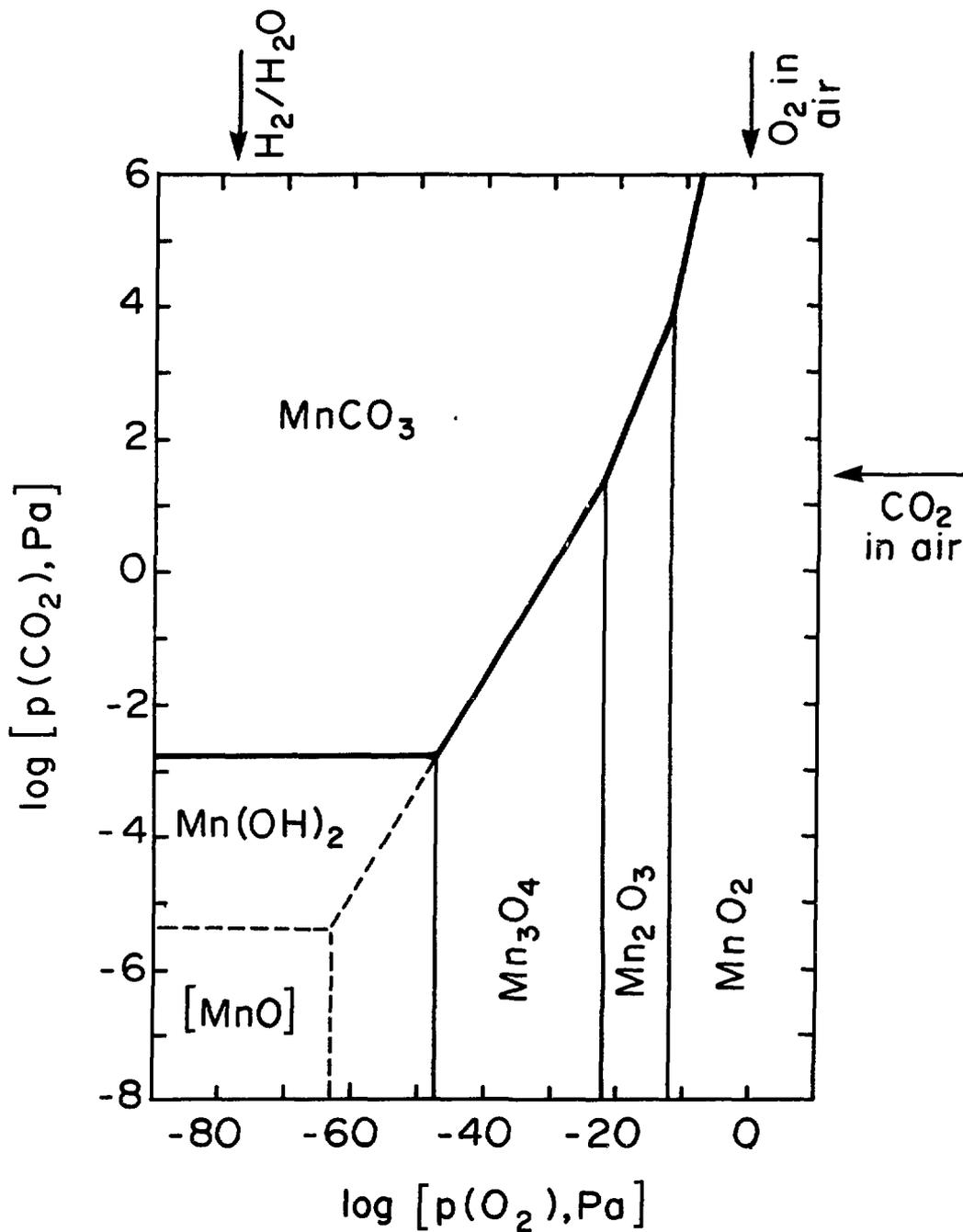


FIGURE 7. Calculated Carbon Dioxide Partial Pressures as a Function of Oxygen Partial Pressure in the System $\text{MnO}-\text{O}_2-\text{CO}_2-\text{H}_2\text{O}$, Based on Equations 47 to 50.

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