

isomers. Molecular mechanics calculations and laboratory experiments have revealed that double bond isomerizations of sterenes in immature sediments occur only via tertiary carbocations (e.g. de Leeuw *et al.*, 1993).

In petroleum geochemistry, the distribution of C₂₇:C₂₈:C₂₉:C₃₀ steranes has been used as an indicator of the source (marine or terrigenous) of the organic matter which produced the oil, and for correlating oils with their source rocks (e.g. Moldowan *et al.*, 1992). Terrestrial-derived oils often show a strong predominance of C₂₉ steranes, presumably reflecting the high abundance of the C₂₉ sterol β -sitosterol (24R-ethylcholesterol) in most higher plants. However, C₂₉ sterols also occur in a variety of marine organisms and so a predominance of C₂₉ sterane isomers is not conclusive evidence that the organic matter is of terrestrial origin (Volkman, 1986). Marine oils often have similar proportions of C₂₇ and C₂₉ steranes with C₂₈ steranes about half as abundant.

C₃₀ steranes rarely comprise more than 10% of the total steranes, but the structure of the side chain and presence of a methyl group at C-4 can provide important information on the source of the oil. The presence of the C₃₀ 24-*n*-propylcholestanes in a petroleum is usually taken to indicate that the oil is derived from a marine source rock (McCaffrey *et al.*, 1994). These steranes are present in oils from the Early Proterozoic (1800 Ma) to the Miocene (15 Ma), but their abundance appears to vary with the age of the source rock. Another group of C₃₀ steranes called dinosteranes (4 α ,23,24-trimethyl-5 α -cholestane) appears to be linked to contributions from dinoflagellates (and their algal progenitors), and indeed a closely related sterol 4 α ,23,24-trimethyl-5 α -cholest-22E-en-3 β -ol (dinosterol) is found in modern-day dinoflagellates (Summons *et al.*, 1992).

The sterane distributions in oils and sediments are routinely determined by electron-impact GC-MS using *m/z* 217 and 218 ions (or *m/z* 231 and 232 for 4-methyl steranes), whereas diasteranes have a major fragment ion at *m/z* 259. More detailed deconvolution of these often exceedingly complex mixtures can be obtained using metastable reaction monitoring GC-MS. The sterol precursors of steranes occur with a single configuration [8 β (H),9 α (H),10 β (CH₃),13 β (CH₃),14 α (H),17 α (H),20R], but during diagenesis and catagenesis the ratios of the two configurations at C-14, C-17 and C-20 change in a systematic fashion. The predominance of biologically derived 20R isomer is gradually lost so that an approximately equal mixture of 20R and 20S isomers occurs in the steranes at maturities well before the oil window. The flat configuration imposed by the 14 α (H),17 α (H) stereochemistry in the sterol is also lost to the thermodynamically more stable 14 β (H),17 β (H) form so that these isomers predominate in mature oils. The ratios of these various isomers can thus be used as indices of thermal maturation although some caution is needed since the sediment matrix and double bond position in the parent sterol can influence the proportions of the various isomers (ten Haven *et al.*, 1986).

Despite many recent advances, our understanding of the geochemistry of steroids is far from complete. Reasonable sources can be proposed for most of the sterols found in aquatic environments, but exceptions continue to be found where unusual sterols are major constituents. The origins of some steroidal compound classes, such as steryl ethers, are still not known. Such examples highlight our imperfect knowledge of carbon sources in some environments. Studies of steranes have also yielded surprising results such as the identification

of steranes containing C₁-C₆ alkyl groups at positions C-2 and C-3 on the steroidal A ring (Summons and Capon, 1991). Naturally occurring sterols with such alkylation patterns are not known, which suggests that these unusual steranes must be formed by diagenetic reactions or by microbial modifications to sedimentary sterenes in young sediments.

The increasing availability of isotope ratio GC-MS systems able to provide $\delta^{13}\text{C}$ values for individual compounds separated by capillary gas chromatography will undoubtedly lead to further studies of steroidal compounds in recent and ancient sediments and crude oils. Our understanding of the sources of organic matter in sediments, our reconstructions of paleoenvironmental conditions and the pathways by which organic matter is broken down in sediments will be further enhanced using this technique.

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Cross-references

- Biomarker: lipid
- Coal: origin and diagenesis
- Diagenesis
- Gas chromatography mass spectrometry (GC-MS)
- Geochemistry of sediments
- Hydrocarbons
- Lipids (eubacteria and archaeobacteria)
- Oil-oil and oil-source rock correlation
- Organic geochemistry
- Organics: contemporary degradation and preservation
- Organics: sources and depositional environments
- Petroleum

STOICHIOMETRY

Introduction

Stoichiometry refers to the molar relationship of elements within a chemical entity, such as a multielemental ion, mole-

cule, or mineral. The definition of stoichiometry can be illustrated with an example based on albite feldspar, a common rock-forming silicate mineral. Albite has the following chemical formula: $\text{NaAlSi}_3\text{O}_8$. The stoichiometry of this formula indicates that 1 mole of albite contains 1 mole of sodium (Na) atoms, 1 mole of aluminum (Al) atoms, 3 moles of silicon (Si) atoms, and 8 moles of oxygen (O) atoms. As a reminder, a mole is defined in terms of Avogadro's number: $6.023 \times 10^{23} \text{ mol}^{-1}$.

Stoichiometry can also be used in reference to the molar relationship between reactants and products for any type of chemical reaction. As an example, the reaction of quartz with water can be represented by the following dissolution (forward) or precipitation (backward) reaction:

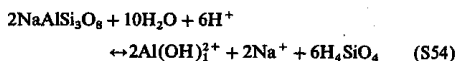


The reaction in the forward direction can be interpreted in terms of 1 mole of quartz reacting with 2 moles of water yielding 1 mole of silicic acid.

The stoichiometric relationship between products and reactants can often yield important information on many varied geochemical processes. In order to illustrate how stoichiometric relationships are applied in geochemistry, the dissolution behavior of albite feldspar under hydrothermal conditions is examined. Stoichiometric ratios between elements are used to deduce information on the preferential release of elements from the structure, the precipitation of secondary phases on the surface, and the exchange of H and Na during the creation of leached/ altered layers.

The preferential release of Na and the formation of leached layers

One can examine the stoichiometry of the dissolution reaction in order to gain insights into the mechanisms of hydrolysis, as well as other processes which occur in parallel or in series with hydrolysis. The dissolution reaction at acid pH can be represented by the following reaction:



If the dissolution process is stoichiometric (also called congruent), then the ratio of Na:Al:Si in solution should equal 1:1:3, this being the stoichiometric ratio of Na:Al:Si in the solid. As discussed below, the dissolution process is not always stoichiometric with respect to time.

Figure S22 shows the dissolution behavior of albite as a function of time at 200°C in an aqueous HCl solution at pH 2.0 (the data discussed below are taken from Hellmann, 1995). The data were acquired in a flow-through reactor (see Hellmann, 1994). The diagram shows the log rate of dissolution in terms of the release rates of Si, Al, and Na. It is important to note that each of the log rates is corrected for the stoichiometry of albite. This quite simply means that the raw release rates for each element are divided by the appropriate stoichiometric factor, which are as follows: Si = 3, Al = 1, and Na = 1. Therefore, the rates shown in Figure S22 are stoichiometrically normalized.

The initial rate of release of Na from the structure exceeds that of Al and Si by slightly more than one order of magnitude. This is referred to as non-stoichiometric or incongruent dissolution. As time progresses, the release rate of Na monotonically

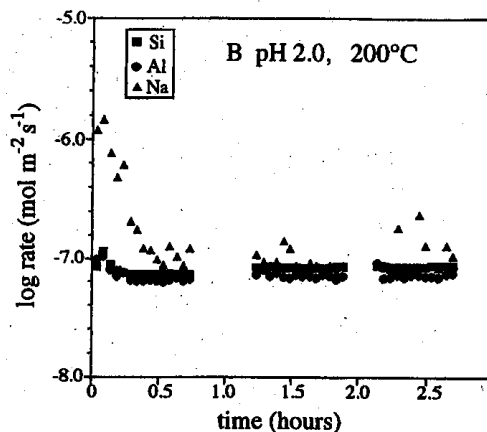


Figure S22 The stoichiometry of albite dissolution at pH 2.0 and 200°C as a function of time. The release rates of Si, Al and Na have all been stoichiometrically normalized, such that the release rates represent the overall dissolution rate of albite. Note the preferential release of Na during the initial stages of dissolution, this leading to the formation of a surface leached layer depleted in Na. Dissolution becomes stoichiometric at time $t > 1$ h (adapted from Hellmann, 1995).

decreases, such that after approximately one hour, the release rates of Na, Al and Si are all roughly equal (within the error of the analyses). At this stage, the dissolution process is characterized as being stoichiometric or congruent.

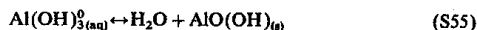
The fact that the initial stages of dissolution are non-stoichiometric has important implications for the mechanisms of dissolution. The initially greater release rate of Na leads to the formation of a near-surface layer that is depleted in Na with respect to the bulk chemical composition of albite. Near-surface layers with a chemical composition (i.e. stoichiometry) different from that of the bulk are termed leached layers. Leached layers commonly form on silicate minerals that have easily exchangeable alkali or alkaline earth elements in the structure, such as is the case with all feldspars (see Hellmann, 1995, and references therein). In addition, the formation of leached layers also results in a more open structure, resembling that of a glass (Casey *et al.*, 1993; Hellmann, 1995).

By following the stoichiometry of dissolution as a function of time, it is possible to calculate the depths of these leached layers. Based on an integration of the Na and Si rate curves shown in Figure S22, the calculated depth of Na leaching equals approximately 1500 Å. In general, leached layer depths are a function of the pH and temperature of the solution. Acid pH conditions and elevated temperatures favor the formation of deep leached layers (several thousands of Å). On the other hand, at neutral pH and low temperature conditions, the dissolution of feldspars does not lead to the formation of leached layers more than ~100 Å thick (see references in Hellmann, 1995).

Evidence for precipitation of a secondary Al surface phase

Figure S23 shows another example of the evolution of the stoichiometry of albite dissolution as a function of time (from Hellmann, 1995) at 300°C in deionized water (pH 5.7). As was the case in the example shown above, Na is preferentially released during the initial stages of dissolution. Note, however, that the degree of preferential leaching is significantly smaller, since the maximum difference between the Na and Si rates of release is much less than an order of magnitude. The calculated depth of the Na depleted layer is ~250 Å.

This same figure also shows that the Al rate curve is significantly below the Na and Si rate curves over an extended period of time. The non-stoichiometric nature of the Al rate can be interpreted in terms of an initially rapid release of Al from the feldspar structure into solution, causing the solubility limit of an Al phase to be exceeded and thereby resulting in the subsequent precipitation of a secondary surface phase. At these conditions, boehmite ($\text{AlO}(\text{OH})_0$) is the most likely Al-bearing phase to precipitate, as shown in the equation below:



The changing slope of the Al rate curve yields important information on two interdependent processes; the rate of Al release from the structure and the rate of Al precipitation. The initial decrease (i.e. negative slope) of the initial Al rates reflects a decreasing rate of Al release from the structure coupled with the precipitation of boehmite, as represented by the forward reaction in eqn (S55).

The minimum in the Al rate curve is due to a transient equilibrium between the rate of Al precipitation and its rate of release. The subsequent rise in the Al rate curve can in turn be interpreted in terms of the rate of Al release exceeding the

rate of precipitation. This is primarily due to the rate of precipitation becoming negligible since the solution is no longer supersaturated with respect to any Al-bearing phases (thus, the backward reaction in eqn (S55) applies). The main reason for this is that the intrinsic rate of Al release from the feldspar structure decreases monotonically with time, in a similar manner to the Na release rate. The undersaturation of the solution with respect to Al in contact with the feldspar leads to the re-dissolution of the precipitated Al surface precipitate. Eventually a steady-state condition is reached where the Al rate becomes constant, and is only a function of the intrinsic rate of Al release from the structure. The equality of the Al, Na and Si release rates denotes that the overall dissolution process is stoichiometric at steady-state conditions.

It is interesting to note that under certain conditions of dissolution, such as at low pH and high temperatures (see Hellmann, 1995), the overall dissolution process may remain non-stoichiometric with respect to Al. This occurs when the rate of release of Al remains sufficiently high such that an Al phase continuously precipitates during the dissolution process (see SEM images of boehmite in Hellmann *et al.*, 1989). The continuous precipitation of an Al phase shows that even though the overall dissolution process is non-stoichiometric, the release rates of Na, Al and Si may all be equal at the actual sites of bond hydrolysis. It is simply the precipitation process at the solid/fluid interface which changes the overall stoichiometric relationships of the released elements. Thus, when the stoichiometry of dissolution is considered, it must be clear whether bond hydrolysis or the overall dissolution process is being referred to.

H and Na exchange reactions

As was previously mentioned, the release of readily exchangeable alkali or alkaline earth elements from the feldspar structure facilitates the formation of leached layers. For the case of

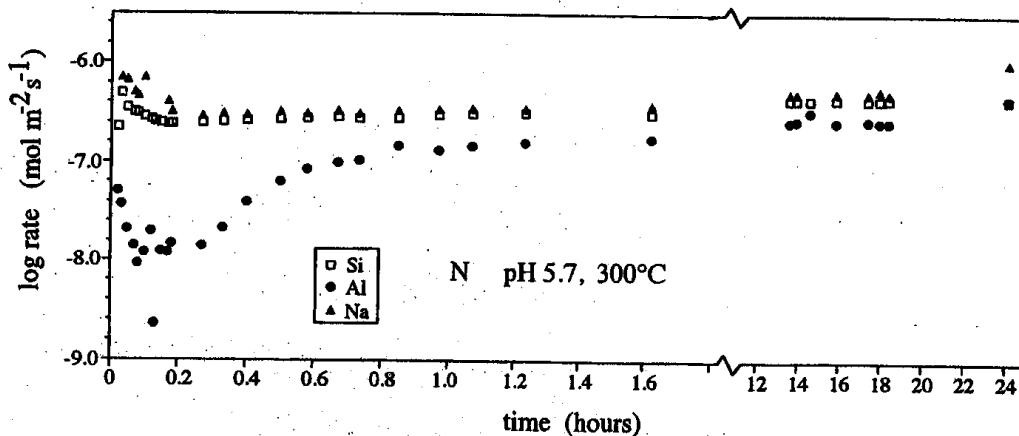
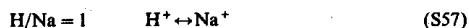
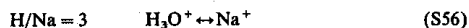


Figure S23 The stoichiometry of albite dissolution at pH 5.7 and 300°C as a function of time. As in Figure S21, the elemental release rates are stoichiometrically normalized. The initial negative slope in the Al rate curve is due to a rapid release of Al at the beginning of dissolution, leading to the transient precipitation of a secondary Al-bearing surface phase. Note that the dissolution process eventually becomes stoichiometric, where the Al rate curve is only a function of the intrinsic rate of Al release from the feldspar structure (adapted from Hellmann, 1995).

albite dissolution at acidic pH conditions, Na^+ ions are exchanged with H ions (either H^+ or H_3O^+). The stoichiometry of the exchange reactions can be used to predict the ratio of incorporated H to released Na (H/Na) which should occur within the albite structure, based on the following reactions occurring within the leached layer:



H/Na ratios equal to 3 or 1 represent pure ion exchange mechanisms (eqns (S53, S57)). On the other hand, a ratio ranging from 1 to 3 is indicative of a mixed mechanism consisting of ion exchange and infiltration of free water molecules, as shown by eqn (S58) (Dran *et al.*, 1988; Petit *et al.*, 1990).

In a recent study based on albite hydrolyzed at 300°C at various pH conditions (Hellmann *et al.*, 1997), H and Na concentrations were measured as a function of depth using a resonant nuclear reaction technique (RNRA). At acidic pH conditions, the measured H/Na levels increase from ~2 at the surface to ~3 at a depth of 1000 Å. At neutral pH the measured H/Na ratios range between ~1.0 and 1.5. The interpretation of these ratios, however, is not straightforward since there are other reactions which control the amount of H incorporated into the structure. The creation of aluminol and silanol groups, and recondensation reactions, are examples of such reactions.

Nonetheless, the above ratios show that the penetration of H species into the structure is quantitatively more important during hydrolysis at acidic pH than at neutral pH conditions. This in turn suggests that leached layers created at acidic pH are structurally more open than those created at neutral pH. This is potentially one reason why dissolution rates for feldspars increase with decreasing pH in the neutral to acidic pH region (see discussion in Hellmann, 1995).

In summary, the above examples serve to show how the stoichiometry of elements can be used to better understand the fundamental processes occurring during the dissolution of feldspars, the most important constituent of the Earth's upper crust. The information provided by examining the stoichiometry of reactions reveals that feldspars (and related silicates) dissolve in a very complex manner; as evidenced by different rates of elemental release, potential surface precipitation reactions, and solid/fluid exchange reactions. Such basic information is necessary for better understanding the chemical evolution and behavior of water-rock systems, such as associated with chemical weathering reactions occurring on the Earth's surface, or due to reactions occurring at depth at elevated temperatures and pressures.

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Cross-references

Acids and bases
Aqueous solutions
Atomic mass unit, Avogadro constant and mole
Chemical kinetics
Clay minerals - ion exchange
Crystal chemistry
Experimental mineralogy and petrology
Geochemical thermodynamics
Hydrothermal solutions
Mineral defects
Mineral genesis
Mineralogy
Phase equilibria
Solid solution
Solubility

STRONTIUM: ELEMENT AND GEOCHEMISTRY

History

Strontium was named for the locality of the lead mine (Strontian, Argyleshire, Scotland) from which, in 1787, a previously rare mineral (strontianite, SrCO_3) was found in abundance. In 1790 Dr Adair Crawford reported on the medicinal properties of the 'muriated barytes' obtained by decomposition of this mineral, concluding, "this mineral really possesses different properties from ... baryta". Sr was isolated by Sir Humphrey Davy in 1808, by the same electrolytic method used to isolate Ca and Ba.

Physical properties

Strontium has the symbol Sr, atomic number 38, atomic mass 86.62, electron configuration $[\text{Kr}] 5s^2$, valence Sr^{2+} , melting point 769°C, boiling point 1384°C. Metallic Sr has 3 low-pressure polymorphs (transitions 235°C and 540°C); the room temperature form is a soft (1.8, Mohs scale), silvery metal, which rapidly oxidizes in air to a yellowish colored oxide, and decomposes water vigorously.

Sr has four stable isotopes: ^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.00%), and ^{88}Sr (82.58%). These proportions vary because ^{87}Sr is the radiogenic daughter of ^{87}Rb (half-life 4.88×10^{10} years); consequently, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are used in geochronology and isotopic tracer studies (see Rubidium-strontium method). In addition, 24 short-lived radioactive isotopes of Sr are