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POTENTIAL BARIUM-STRONTIUM GEOTHERMOMETRY

TRAVERTINE DEPOSITS

Introduction

Travertine is a calcium carbonate deposit which forms by precipitation from ground water and mineral springs. The travertine rock commonly forms in wide open spaces, such as limestone caves, producing stalactites and stalagnites. Such deposits are assumed to be due to supersaturation of slow-forming droplets brought about by partial evaporation. The ground water from which these deposits form is assumed to be cool.

Of more immediate interest are those travertine deposits found in veins or associated with warm spring deposits. These deposits may be associated with silicious sinter or opaline quartz. The sinter or opaline quartz should also have a geochemical signature that is amenable to chemical geothermometry.

Practical application of a travertine Ba-Sr geothermometer

Travertine, sinter and opaline quartz are common rock/mineral manifestations of near-surface geothermal systems. They are formed as a result of reduced solubility brought about by decreases in either pressure or temperature of the thermal system. The precipitation of calcite, the major constituent of travertine, results in the selective removal of cations which are chemically similar to calcium. The quantity of trace elements removed from solution should reflect the composition of the thermal waters at the time of deposition.

Deposition of precipitates from thermal waters tends to block the conduits and restrict flow from the source to the surface. Complete blockage will result in either a capped thermal system or the development of new conduits. New conduits will provide immediate sites for direct evaluation of the geothermal system whereas capped systems do not.

A second case in which travertine deposits are found without associated hot spring activity comes about when changes in the ground water table or flow regime interrupt the interaction between heat source and ground water.



Since surface travertine deposits are geologically short-lived phenomena, any evaluation technique which provides paleogeothermal temperatures should also provide an approximation of present-day geothermal temperatures. A procedure for evaluating the potential of such a chemical geothermometer is presented.

Theoretical considerations in support of a Ba-Sr geothermometer

Elevated temperatures and pressures such as those associated with magmatic events promote free substitution among different sized ions (or atoms) in crystal lattices. For example, a reaction involving NaCl and KCl at 800°C forms a continuous series of mixed crystals. Lower reactive temperatures decrease this solid miscibility. The same reactants at 20°C form discreet NaCl and KCl crystals with practically no solid miscibility between dissimilar cations.

Another example of this decrease in miscibility with decrease in temperature is found in the study of barium and strontium. Primary minerals of these elements are never formed from magmatic melts because the two elements in question enter into crystal lattices of calcium-bearing and potassium-bearing minerals at the time of crystallization. Discreet mineral forms of barium and strontium separate from aqueous solutions at low temperatures because of the decrease in possibility of forming mixed crystals.

Following the relationship between mixed crystal formation and temperature one step further, one can readily envision an analogous situation in which the relative concentrations of cations in an aqueous solution will change with decrease in temperature. Such is the basis for development of the empirical geothermometers involving relative concentrations of potassium, calcium and sodium.

The success of a chemical geothermometer depends upon the change in concentration, or relative concentrations, with temperature. The element or elements employed in the thermal calculations should be of the common variety and easily analyzed. Complicating side reactions and extraneous variables with poorly defined parameters are other features which must be evaluated prior to the selection of a chemical geothermometer.

Of prime importance in developing a chemical geothermometer is the selection of elements with characteristics amenable to this type of calculations. Such characteristics would include: (1) group 1 (Fig.1); (2) full substitution; (3) high solubility-temperature gradient; (4) easily analyzed; (5) naturally abundant; (6) low solubility of final mineral product.



All elements may be divided into three groups: (1) those which remain in ionic solution over a wide range of pH values; (2) those which precipitate by hydrolysis; and (3) those which form complex anions contain oxygen which usually produce ionic solutions. The ionic potential of an element is the prime value which determines the group to which it belongs. Table I lists a few of the more common elements and their ionic potential while Figure I is a graphic illustration of the grouping of these elements. All of the metals thus far used in chemical geothermometry calculations fall into group I as do the two proposed for this study.

Methods of evaluating the travertine Ba-Sr geothermometer

- I. Search the literature for background information on the behavior of Ba and Sr in environments of elevated temperature. Thermochemical values need to be obtained prior to construction of a theoretical relationship.
- II. Develop a theoretical model based on the thermodynamic information from step I. Check the model against published travertine data.
- III. Evaluate the proposed model against first-hand field data from modern travertine deposits associated with measurable geothermal springs.
- IV. Publish results.



Table 1 Common elements and their Ionic Potentials

Ionic Potentials *

Cs ¹⁺	0.61	Sm ³⁺	2.7	Ti ⁴⁺	6.3
Rb ¹⁺	0.67	Y ³⁺	2.8	Nb ⁵⁺	7.3
K ¹⁺	0.71	Lu ³⁺	3.0	Mo ⁶⁺	9.7
Na ¹⁺	1.0	Sc ³⁺	3.6	Si ⁴⁺	10
Li ¹⁺	1.3	Th ⁴⁺	3.7	B ³⁺	15
Ba ²⁺	1.4	Ce ⁴⁺	3.9	P ⁵⁺	15
Sr ²⁺	1.6	Zr ⁴⁺	4.6	S ⁶⁺	20
Ca ²⁺	1.9	Al ³⁺	5.3	C ⁴⁺	27
Mg ²⁺	2.6	Be ²⁺	5.9	N ⁵⁺	45

* Ionic Potential = $\frac{\text{ionic charge}}{\text{ionic radius}}$

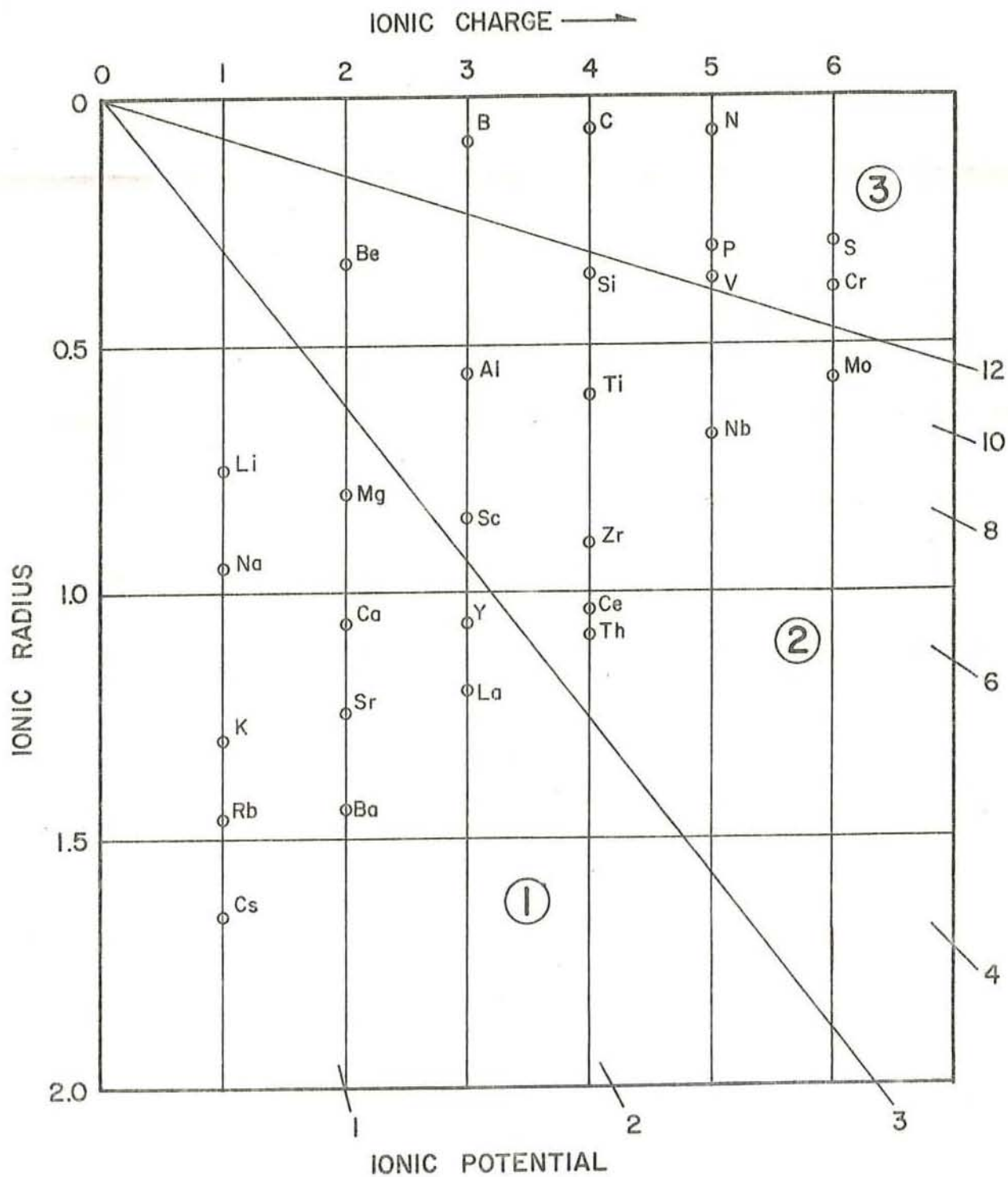


FIGURE 1. Distribution of selected chemical elements by ionic radius and charge.