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*The Physicochemical Basis
of the Na-K-Ca Geothermometer*

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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D. R. Janecky
R. W. Charles
G. K. Bayhurst
T. M. Benjamin

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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THE PHYSICOCHEMICAL BASIS OF THE Na-K-Ca GEOTHERMOMETER

D. R. Janecky, R. W. Charles, G. K. Bayhurst, and T. M. Benjamin

ABSTRACT

Regular changes in solution composition were observed experimentally during granite reaction with dilute NaCl (+CaCl₂) solutions; these changes closely follow the empirical Na-K-Ca geothermometer relationship. Initial minerals forming the granite (quartz, plagioclase, K-feldspar, and biotite) were etched by the reactions. Alteration phases formed include calcium-zeolite at <300°C, feldspar overgrowths at >300°C, and minor amounts of clay and calcsilicate at all temperatures. Amphibole overgrowths were also found at 340°C. Quartz is near saturation in all experiments, and preliminary calculations of aqueous species distributions and mineral affinities indicate that the solutions achieve super-saturation with feldspars as the temperatures increase. A consistent variation attributable to pH differences was observed in the empirical geothermometer relationship for all experimental data. At 340°C, the experimental solutions appear to have deviated slightly from the empirical Na-K-Ca relationship. Such deviations may also be found in natural systems that attain such temperatures.

I. IMPORTANCE

The Na-K-Ca geothermometer is an important tool used in exploration for geothermal resources. It was defined empirically from measured solution compositions and maximum measured or estimated temperatures from a variety of geothermal systems.¹ However, the mineral reactions controlling solution compositions as a function of temperature are not clearly evident.¹⁻³ Although experimental investigation of reaction mechanisms and alteration mineralogy in controlled systems has not yet been done, such investigations can help define the limits of the geothermometer's applicability with respect to temperature

and rock composition. In addition, experimental data can be used to refine and evaluate the empirical relationship, particularly at temperatures above 300°C, where data on natural systems is limited and more uncertain.

Information on alteration minerals in equilibrium with solutions of known composition, at known temperatures, is important in evaluating active geothermal systems, and it can also be used to correlate extinct geothermal systems with known active systems. Such correlations would allow a more detailed understanding of temperature distribution and solution compositions in old or extinct systems; thus, they would be important in examining and evaluating areas for potential ore deposits or determining the previous hydrothermal history of areas being considered for nuclear waste disposal.

II. BACKGROUND

Solutions used to define the empirical Na-K-Ca geothermometer¹ have variable salinities (0.002 to 4.0 molal total dissolved salts) and temperatures (4 to 340°C). The predominant anion is chloride, and the empirical relationship does not give reasonable results for carbonate-rich^{4,5} or acid-sulfate solutions.¹ Rock types involved in the geothermal systems vary from silicic volcanic and sedimentary assemblages to basalt. It has been suggested that feldspars control the concentrations of sodium and potassium in most natural hydrothermal solutions,^{1,6,7} whereas calcite solubility is thought to control the absolute quantity of calcium in solution.¹ Free silica as quartz, chalcedony, or cristobalite is assumed present in all systems;¹ however, the range of rock types that fit the empirical relationship does not require such an assumption—only that enough silica and aluminum be available to form sodium-, potassium-, and calcium-bearing minerals. For most applications, quartz-bearing rocks are an important or dominant component of the system.

A variety of chemical geothermometers have been and continue to be proposed in the literature—for example, a sodium/lithium geothermometer for low-temperature systems,⁸ and gas geothermometers⁹ for carbonate-rich systems. In addition, several refinements of the Na-K-Ca geothermometer have been presented that deal with solutions containing significant concentrations of magnesium¹⁰ or attempt to correct for carbonate-rich waters.⁴ However, since their formulation, the Na-K-Ca geothermometer and the silica geothermometer have proved to be useful, reasonably accurate, and generally applicable for geothermal systems that have reservoir temperatures above ~150°C.

III. APPROACH

To examine alteration mineralogy and the Na-K-Ca geothermometer for silicic rocks in the high-temperature range of its applicability, disks of Westerly Granite were reacted with 10-millimolal NaCl solutions at temperatures of 260, 280, 300, 320, and 340°C. In parallel experiments, 0.1 millimolal of CaCl₂ was added to the reactant solution to examine the reversibility of the reactions. Most reactions were run in flexible gold-titanium reaction-cell hydrothermal equipment^{11,12} at 272 bars total pressure. In addition, one experiment was run in a recirculating reaction system.¹³ During the experiments, solution samples

were extracted and analyzed for total sodium, potassium, calcium, aluminum, silica, and iron by plasma emission spectroscopy, chloride and sulfate by ion chromatography, $\text{pH}_{25^\circ\text{C}}$ by specific ion electrode, and total carbonate by infrared adsorption. The rock disks were removed from the reaction cells at the conclusion of the experiments and examined for alteration products by optical and electron microscopy, electron microprobe, proton microprobe, and x-ray diffraction.

IV. SIGNIFICANT RESULTS

The experimental data for $\text{pH}_{25^\circ\text{C}}$ sodium, potassium, calcium, and aluminum show consistent variations with respect to temperature in both the Na-Cl and Na-Ca-Cl solution experiments (Figs. 1 and 2). Sodium and chlorine concentrations in solution were relatively unchanged by the experiments, whereas potassium increased with temperature and calcium decreased (Figs. 1 and 2). The initial solutions, which include 0.1-millimolal calcium, also have an initially lower $\text{pH}_{25^\circ\text{C}}$ of 2.9 (*vs* 6.1 for the NaCl solution). Most of the pH difference is neutralized by the reaction with the rock; however, the Na-Ca-Cl solution reactions are ~ 0.5 unit more acid at steady state, and they contain ~ 0.75 log unit more calcium and slightly less dissolved aluminum than the Na-Cl solution experiments do. Aluminum in solution does not appear to vary significantly with respect to temperature (within analytical uncertainties), except at the highest temperatures, where it decreases slightly. Total carbonate in solution after reaction with the granite disks increased from the initial solution compositions and also increased with temperature (see Table). The Na-Ca-Cl experiments reached higher concentrations of carbonate than did Na-Cl experiments (see Table), which is consistent with relative calcium concentrations and control by calcite dissolution. The circulation system at 300°C had significantly lower total carbonate and calcium than did the static systems (see Table and Figs. 1 to 3), possibly because of precipitation in the ambient temperature section of the flow path. Dissolved silica in the flexible cell experiments increased slightly with temperature—at or slightly above quartz saturation—with the exception of early samples (Fig. 4). Samples from circulation reaction systems, however, are consistently slightly undersaturated with quartz (Fig. 4).

Two types of alteration phases were observed on the surfaces of the granite disks. At temperatures of 300°C and lower, the most commonly observed alteration phase was a zeolite with small amounts of clay and calcsilicate minerals. At 300°C and greater, zeolites were not observed, but overgrowths on feldspars were common. These higher temperature runs also contained clay, calcsilicate minerals, and amphibole overgrowths. Primary quartz and feldspars were etched in all experiments, and alteration products were rarely observed on quartz. Semiquantitative analyses of the alteration phases by SEM-EDAX indicate that the primary cation in the zeolites is calcium and the bulk composition may be that of faujasite. The calcsilicate is low in aluminum, magnesium, and iron and may be truscottite or a similar mineral. Where it is observed in thin sections cut across the altered disks, the calcsilicate grows as crystal sprays on calcite exposed at

Fig. 1. Concentrations of sodium, potassium, calcium, and aluminum and $\text{pH}_{25^\circ\text{C}}$ during reaction of Westerly Granite disks and 10-millimolar NaCl solution as a function of temperature. The solid line associated with pH data represents neutrality under experimental conditions.

the surface. Clay minerals can grow on any initial phases and are rich in iron, magnesium, and calcium. Iron is present in excess of any reasonable clay structure and, therefore, must also be contained in an intergrown oxide phase. The feldspar overgrowths are apparently albitic and occur on both K-feldspar and plagioclase. Amphibole overgrowths containing calcium, iron, magnesium, and aluminum were also observed and analysed. Preliminary calculation of mineral stabilities with respect to the solution samples indicates that calcite was undersaturated and that feldspars were undersaturated at the lowest temperatures but became supersaturated at or above 300°C .

Calculation of the experimental Na-K-Ca relationship used for the Na-K-Ca geothermometer reveals that the experiments closely duplicate the empirical relationship, particularly at temperatures of 300°C and below (Fig. 5a). At 340°C , where significant

Fig. 2. Concentrations of sodium, potassium, calcium, and aluminum and $\text{pH}_{25^\circ\text{C}}$ during reaction of Westerly Granite disks and 10-millimolar NaCl plus 0.1 millimolar CaCl_2 solution as a function of temperature. The solid line associated with pH data represents neutrality under experimental conditions.

TOTAL CARBONATE CONCENTRATIONS IN MILLIMOLAL

Experiment	Temperature (°C)			Initial Solution Composition
	260	300	340	
Na-Cl	1.5		2.5	1.2
Na-Ca-Cl	1.5	3.2	5.5	0.
circulation		0.3		1.2

Fig. 3. Concentrations of sodium, potassium, calcium, and aluminum, and $\text{pH}_{25^\circ\text{C}}$ during reaction of Westerly Granite disks and 10-millimolal NaCl solution in a circulation system as a function of temperature. The solid line associated with pH data represents neutrality under experimental conditions.

overgrowths of feldspar were observed in the experiments, however, the experimental data may indicate a steepening of the empirical relationship. The experimental data also indicate that pH variations may affect the geothermometer in a consistent manner; the more acid Na-Ca-Cl solution experimental data plot consistently above the Na-Cl solution data (Fig. 5b). Few samples of active geothermal systems existed at such temperatures when the geothermometer was initially defined. However, evaluation of more recent samples from hotter systems (temperatures above 300°C) and examination of alteration studies in light of this new data may confirm the significance of the solution composition and alteration patterns observed in these experiments.

Fig. 4. Concentration of silica in solution during reaction of Westerly Granite disks with (1) NaCl solution in flexible-cell reaction equipment (hexagons) and circulating system equipment (pluses) and (2) Na-Ca-Cl solution in flexible-cell reaction equipment (triangles). The solid line indicates quartz solubility under the conditions of the experiments.

V. CONCLUSIONS

Regular changes in solution composition were observed experimentally during granite reaction with dilute NaCl (+CaCl₂) solutions; these changes closely follow the empirical Na-K-Ca geothermometer relationship.¹ Initial minerals forming the granite (quartz, plagioclase, K-feldspar, and biotite) were etched by the reactions. Alteration phases formed include calcium-zeolite at <300°C, feldspar overgrowths at >300°C, and minor amounts of clay and calcsilicate at all temperatures. Amphibole overgrowths were also found at 340°C. Quartz is near saturation in all experiments, and preliminary calculations of aqueous species distributions and mineral affinities indicate that the solutions achieve super-saturation with feldspars as the temperatures increase. A consistent variation,

Fig. 5. (a) The primary line indicates the relationship used to define the empirical Na-K-Ca geothermometer from natural systems (open symbols);¹ the experimental data from this work are superimposed. (b) Experimental data from this work are plotted with respect to Na-K-Ca geothermometer relationship (heavy line).¹ Estimated fits of experimental data (light lines) shift as a function of pH differences and indicate an experimental increased slope above 300°C , which correlates with changes in alteration assemblages.

attributable to pH differences, was observed in the empirical geothermometer relationship for all experimental data. At 340°C, the experimental solutions appear to have deviated slightly from the empirical Na-K-Ca relationship. Such deviations may also be found in natural systems that attain such temperatures.

This project is part of a series of studies dealing with hydrothermal reactions between silicic rocks and dilute-to-concentrated chloride solutions. These studies attempt to quantify reaction pathways, minor- and trace-element exchange and mobility, and controls on alteration mineral assemblages. The understanding gained from experimental and theoretical investigations can be applied to understanding and interpreting results from geothermal exploration, Continental Scientific Drilling Projects in both active (for example, Salton Sea Geothermal System, Valles Cauldera, Long Valley) and extinct (for example, the proposed drilling project in the Creede Cauldera) geothermal systems, and characterization of areas to determine the hydrothermal history (for example, Yucca Mountain, Nevada, which is the subject of the Nevada Nuclear Waste Storage Investigations Project).

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