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mospheric waves excited by the 1991 Pinatubo eruption were coupled to the solid Earth, and detailed studies of these coupled waves with the global seismic network provided a means for estimating the total thermal energy emitted by the eruption (10). The deformation associated with the 1994 Northridge earthquake caused significant perturbation to the ionosphere (11). The tsunami excited by the 1968 Tokachi-Oki, Japan, earthquake caused ionospheric disturbances, which suggest the use of ionospheric

measurements for mapping the tsunami wave field in the ocean, which in turn could be used for tsunami warning purposes (12).

The observations reported in these recent papers encourage enhanced efforts toward understanding the geophysical processes involving both the atmosphere and solid Earth. Reports on disturbances in the ionosphere before large earthquakes are numerous (13), but the physics is poorly understood and skepticism prevails. A better understanding of the physics of the lithosphere-atmosphere energy coupling will be a key to resolving these mysterious observations.

References

1. N. Suda *et al.*, *Science* **279**, 2089 (1998).
2. A. E. H. Love, *Some Problems of Geodynamics* (Dover, New York, 1911).
3. K. E. Bullen, *An Introduction to the Theory of Seismology* (Cambridge Univ. Press, Cambridge, 1963).
4. H. Benioff, J. C. Harrison, L. LaCoste, W. H. Munk, L. B. Slichter, *J. Geophys. Res.* **64**, 1334 (1959).
5. K. Nawa *et al.*, *Earth Planets Space* **50**, 3 (1998).
6. N. Kobayashi, and K. Nishida, in preparation.
7. T. Tanimoto, *Geophys. J. Int.*, in press.
8. P. Goldreich and D. A. Keeley, *Astrophys. J.* **212**, 243 (1977).
9. Y. Fukao *et al.*, in *New Images of the Earth's Interior Through Long-Term Ocean-Floor Observations*, Y. Fukao *et al.*, Eds. (Ocean Hemisphere Project, Chiba, 1997), pp. 184–185.
10. H. Kanamori and H. Mori, *Geophys. Res. Lett.* **19**, 721 (1992); R. Widmer and W. Zurn, *ibid.*, p. 765; S. Watada, thesis, California Institute of Technology (1995), p. 118; P. Lognonne, E. Clevede, H. Kanamori, *Geophys. J. Int.*, in press.
11. E. Calais and J. B. Minster, *Geophys. Res. Lett.* **22**, 1045 (1995).
12. K. Najita, P. F. Weaver, P. C. Yuen, *Proc. IEEE* **62**, 563 (1974).
13. M. Gokhberg *et al.*, *Earthquake Prediction: Seismo-Electromagnetic Phenomena* (Gordon and Breach, Amsterdam, 1995).

GEOCHEMISTRY

Origins of Hydrothermal Ores

H. L. Barnes and A. W. Rose

The dominance of hydrothermal deposits as major industrial sources of many elements has stimulated intense study of their genesis for over a century. Their origin is unequivocally by precipitation from aqueous solutions within the upper several kilometers of the crust. Typical close association with active magmatism or deep sedimentary basins implies that these are the heat sources that warm the transporting fluids (see figure). Ore deposition takes place from rising hot solutions at a range of temperatures that extends above 600°C. The challenge has been to unravel the complex chemical and physical processes, including interaction with complicated and varied geology, during extraction of the ore components from source rocks, component transport, and then precipitation of the ores. The fragmentary evidence of these processes is characteristically ancient, perhaps several billion years old, and has been damaged by subsequent geologic events. Our objective continues to be to create ever more accurate models of ore formation not only as an intellectual exercise but also to guide mineral exploration. On page 2091 of this issue, Audétat *et al.* (1) report experimental results that increase our confidence in such models. Several types of information provide the principal bases for current genetic models.

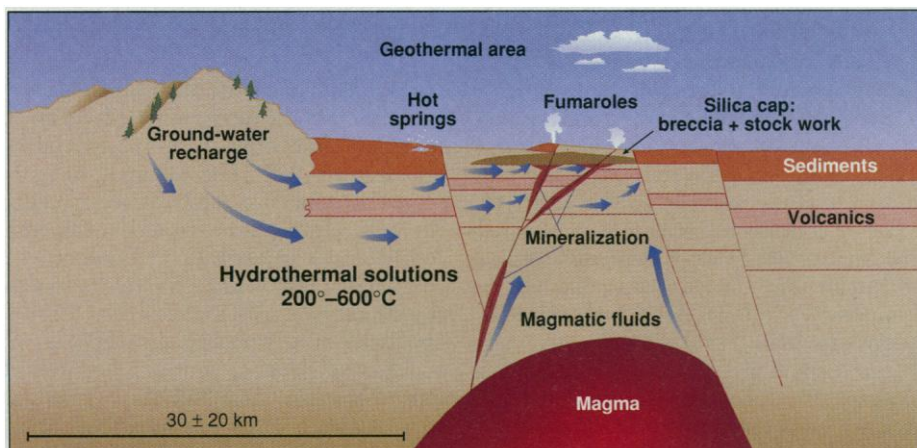
1) Mineral compositions, both isotopic and elemental, provide several clues. The isotopes of 15 elements often identify the source rocks, their ages, and the time of mineralization (2). Thermodynamic stability and measured or calculated solubility of the mineral assemblages limit the processes contributing components to the ore solution, the chemistry of transport, and the conditions and causes of deposition (3).

Many heavy metals occur in ores as sulfides or oxides that are insoluble under most conditions. Laboratory experiments at hy-

drothermal temperatures, in combination with chemical modeling, show that chemical complexing with Cl and S and favorable pH and redox state are the main controls on solubility. Solubilities can now be calculated thermodynamically for most important ore metals at most depositing and transporting conditions to at least 350°C (4).

Solubility behavior indicates the possible physical and chemical processes that could cause precipitation from the fluid, including cooling, reaction with wall rocks (such as neutralization of an acid solution encountering limestone, or an oxidized solution encountering reducing organic matter), exsolution of gases such as H₂S or CO₂ because of decreased pressure, and mixing with cooler water of different chemistry.

2) Fluid inclusions offer samples of the fluids passing through the deposit and, often, approximations of the associated tem-



Valuable deposits. Schematic section of a geothermal system and associated ores. Magmatic and heated ground waters flow upward, possibly depositing ore as a result of cooling or reaction with wall rock. It mixes with heated ground water and boils, causing ore deposition as a result of cooling, chemical change, and loss of volatiles. The ground-water circulation system may occupy 20 to 30 km², with a discharge of 10⁶ to 10⁸ m³ per year. The system may be active for 10,000 to 30,000 years, or longer if additional magma is intruded. [Adapted from figure 14.2 of (9)]

The authors are in the Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA. E-mail: barnes@geosc.psu.edu



peratures and pressures (5). Trapping temperatures of fluid inclusions have been extensively determined by the observation of thin sections of a hydrothermal mineral as it is heated until the vapor and liquid observed at low temperature homogenizes into a single fluid. Such data generally show a wide range of temperatures in single deposits, and a few detailed studies show a complex temperature history during deposit formation (6). Chemical analyses of bulk solutions freed by laboratory crushing of hundreds of inclusions show that Na, Cl with lesser Ca, Mg, K, and sometimes major CO₂ are the major solutes. A few determinations of heavy metals in these bulk samples show tens of parts per million of Zn, Pb, Mn, and similar elements, but few direct determinations of heavy metal concentrations have been available. Changes of fluid chemistry with time remain a problem. Observations on layered veins and crystals, veins cross-cutting other veins, and similar features show that temperature, pressure, and chemical composition during hydrothermal precipitation vary in a highly complex manner, but most previous studies are only able to distinguish a few gross stages.

3) An especially informative contribution to genetic models has come from the study of modern geothermal systems (7–9). These systems are now believed to be modern analogs of ore-forming hydrothermal systems and sometimes deposit subeconomic- to ore-grade concentrations of, in particular, Hg, W, Ag, Au, and Sb (9). Data have been compiled on flow paths and rates for the hot solution along obvious faults and fractures, or through a myriad of small fractures or a porous permeable rock unit. Major flow along a restricted channel is generally favorable for the formation of a large high-grade deposit.

Quantitative models of the extraction of ore components from source rocks, of transport chemistry and flow dynamics, and of causes of deposition have been derived through the combination of thermodynamically calculated mineral stability and solubility, fluid inclusion temperature, and gross major solute data, isotopic data, and geothermal characteristics. However, the actual processes were more complex, and many assumptions were necessary in order to derive these models. Consequently, there remains an uncomfortable uncertainty about their accuracy.

Audétat *et al.* (1), using a new analytical method, resolve that uncertainty for one deposit and furnish a method applicable to many more. They used a laser drill to open individual inclusions directly into a mass spectrometer for analysis of the tiny (10⁻⁸ to 10⁻¹¹ g) solution in the individual inclusions from a 27-step time sequence in a tin-bearing vein from Australia. Chemical concentrations in solution varied in the sequence by factors of more than 1000. The extremely

high but variable temperatures of about 600°C, combined with ratios of different elements, imply precipitation of the early stages from several pulses of boiling magmatic fluid (>600°C). However, the detail of their data shows that the key to tin precipitation was the mixing of cool, dilute water with the hot solution during a late stage of the process. Analyses of associated vapor-rich inclusions, representing trapped vapor from the boiling solution, show that B and Cu were transported in this phase rather than by the liquid hydrothermal solution, as found elsewhere (10). The result is a reassuring confirmation, with much greater detail, of older models for the formation of tin deposits.

This analytical technique, applied to samples carefully studied by other methods, will allow a new level of understanding of temporal variations in hydrothermal chemistry and of the ore-depositing processes in

the many types and variants of hydrothermal ores. Solubility of minor and trace elements at high temperature in real hydrothermal solutions can also be verified and extended.

References

1. A. Audétat, D. Günther, C. A. Heinrich, *Science* **279**, 2091 (1998).
2. H. L. Barnes, Ed., *Geochemistry of Hydrothermal Ore Deposits* (Wiley, New York, ed. 3, 1997).
3. T. M. Seward and H. L. Barnes, in (2), pp. 435–486; J. D. Rimstidt, in (2), pp. 487–516.
4. M. A. McKibben, A. E. Williams, G. E. M. Hall, *Econ. Geol.* **85**, 1926 (1990).
5. E. Roedder and R. J. Bodnar, in (2), pp. 657–698.
6. H. Ohmoto, R. O. Rye, *Econ. Geol.* **65**, 417 (1970).
7. M. A. McKibben and L. A. Hardie, in (2), pp. 877–936.
8. S. D. Scott, in (2), pp. 797–876.
9. H. L. Barnes and T. M. Seward, in (2), pp. 699–736.
10. S. A. Wood, *Seventh Annual V.M. Goldschmidt Conference* (Lunar and Planetary Institute, Houston, TX, 1997), p. 220 (abstr).

SUPERFLUID HELIUM

The Ultimate Spectroscopic Matrix?

K. K. Lehmann and G. Scoles

When chemists need to study unstable species, they resort to one of two methods. They can either produce and study the unstable species in a molecular beam or they can prepare and store the species in a frozen matrix (typically a film of solid argon deposited on a cold window inserted in a spectrometer). In the former method, perturbations are minimized, but synthetic flexibility is limited, whereas in matrix spectroscopy, the opposite is true: many different species can be prepared (1), but perturbations from the matrix that cause inhomogeneous broadening can hardly be avoided. In spite of the limitations, both methods have had a dramatic impact on the development of modern chemistry. On page 2083 of this issue, Grebenev *et al.* (2) report results that disentangle an important unresolved question that arises when these two methods are combined in what is called helium cluster beam isolation spectroscopy.

In fact, one way to minimize matrix-induced perturbations is to use solid or liquid helium as the host matrix. The main problem here is the injection of the condensable sample into the extremely cold matrix without causing aggregation or condensation on the container walls. This is normally

achieved by laser ablation of a sample located in or near the solid or liquid helium matrix (3). Here too, however, sample aggregation and stability remain sources of problems.

In recent years, a synthesis of molecular beams with matrix spectroscopy has been developed that appears to contain the solution to the problems described above. In this method (see figure), a beam of large noble gas clusters, each containing 10³ to 10⁵ atoms, picks up in flight (without being deflected) one or more atoms or molecules, which can then be studied downstream by laser spectroscopy (4). This technique has grown in importance since being extended to liquid helium clusters (5) and especially since the group of Toennies in Göttingen showed that a large variety of impurity molecules inside ⁴He clusters give spectra indicative of free molecular rotation instead of the diffusive rotational or librational motions expected for condensed-phase molecules (6). Although it was previously observed that light molecules with weak anisotropic interactions (such as H₂ or CH₄) could freely rotate in the condensed phase, this was the first time that heavy molecules with high anisotropy, such as the dimer of SF₆, were observed to freely rotate in a liquid medium, albeit with an increased moment of inertia (7). The possibility of resolving rotational molecular spectra in superfluid helium clusters couples the syn-

The authors are in the Chemistry Department, Princeton University, Princeton, NJ 08544-6746, USA.
E-mail: gscoles@princeton.edu